*Maximal groups of automorphisms of compact Riemann surfaces in various classes of finite groups**

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RESUMEN

Dada una superficie de Riemann compacta de género g y una clase de grupos finitos $\mathscr{F}$ es natural buscar una cota para el orden de un $\mathscr{F}$-grupo de automorfismos en términos de g, así como una caracterización de los g para los que estas cotas se alcanzan. Junto a algunos resulados conocidos en torno a estos problemas para varias clases de grupos finitos, hallamos aquí la oportunidad de presentar algunos nuevos. Damos pruebas originales y directas de resultados de Wiman y Maclachlan sobre las cotas $2(2g + 1)$ y $2(2g + 2)$ para grupos cíclicos y abelianos respectivamente. Presentamos nuevas series de g para que las conocidas cotas $16(g - 1)$ y $48(g - 1)$, para grupos metabelianos y solubles respectivamente, se alcanzan. Asimismo enunciamos nuevos resultados acerca del problema en cuestión, que hemos obtenido recientemente para grupos supersolubles y solubles de grado 3.

1. INTRODUCTION

It is well known that a finite group can ben represented as a group of automorphisms of a compact Riemann surface. Let for an integer $g \geq 2$ and a class $\mathscr{F}$ of finite groups, $N(g, \mathscr{F})$ denote the order of the largest group in $\mathscr{F}$ that a compact Riemann surface of genus g admits as a group of automorphisms. Having a class $\mathscr{F}$ of finite groups it is natural to ask for a bound for $N(g, \mathscr{F})$ a well as for the characterizations of those g for which this bound is attained. For the classes of all finite, cyclic, abelian, nilpotent, p-groups (given p), soluble, metabelian, and finally for supersoluble groups an upper bound for $N(g, \mathscr{F})$ as well as infinite series of g for which this bound is attained were found in [4, 5, 6, 11, 12, 13, 14, 17, 18], [10], [15], [19], [20], [1, 2], [3], and [7] respectively. This paper is a survey of results concerning this problems published in recent years. We present some new proofs of known results, strenght and generalize some of them as well as present new results not published yet.

2. PRELIMINARES

In the theory of Riemann surfaces and their automorphisms groups, Fuchsian groups play a very important role. A *Fuchsian group* is a discrete subgroup Γ of

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isometries of the upper half plane D with hyperbolic structure. If D/Γ is a compact surface then Γ has a presentation of the form

$$(x_1, ..., x_r, a_1, b_1, ..., a_g, b_g: x_i^m \ (i = 1, ..., r), \prod_{i=1}^{r} x_i \prod_{i=1}^{g} (a_i\, b_i\, a_i^{-1}\, b_i^{-1}) \tag{2.1}$$

and is said to have a *signature*

$$(g;\, m_1, ..., m_r) \tag{2.2}$$

or to be a Fuchsian $(g; m_1, ..., m_r)$-*group*. The integers $m_1, ..., m_r$ are called *periods* of Γ, and g the *genus*. If $g = 0$ then for brevity we will denote the signature of Γ by $(m_1, ..., m_r)$ and if in addition $r = 3$ we will call Γ a *triangle group*.

Every Fuchsian group Γ has a *fundamental region* associated whose hyperbolic area depends only on the group and thus can be denoted by $\mu(\Gamma)$ and called the area of the group. If Γ has signature (2.2) then

$$\mu(\Gamma) = 2\pi\,[(2g - 2) + \sum_{i=1}^{r} (1 - 1/m_i)] \tag{2.3}$$

and in addition for a subgroup Γ_1 of finite index the following Riemann-Hurwitz index formula holds

$$\mu(\Gamma_1)/\mu(\Gamma) = [\Gamma : \Gamma_1] \tag{2.4}$$

By the uniformization theorem a compact Riemann surface X of genus $g \geq 2$ can be represented as D/Γ, where Γ is a Fuchsian group with signature $(g; -)$ called the *surface group of genus g*. Moreover given such represented surface, a finite group G is a group of its automorphism if and only if there exists a Fuchsian group Λ and a homomorphism Θ from Λ onto G having Γ as the kernel. Such homomorphism is said to be a *surface-kernel homomorphism* and a group G represented in such a form a *surface-kernel factor group of* Λ while Λ is said to *admit G as a surface-kernel factor group*.

It is also well known that a homomorphism from Λ onto G is a surface-kernel homomorphism if and only if it preserves the periods of Λ.

Remark

We see that given a class of finite groups $\mathscr{F}$ the problem of finding the bound for $N(g, \mathscr{F})$ is equivalent to the problem of finding a Fuchsian group with minimal fundamental region that admits a group in $\mathscr{F}$ as a surface-kernel factor group.

3. FINITE GROUPS OF AUTOMORPHISMS OF COMPACT RIEMANN SURFACES

Hurwitz [11] stated that a compact Riemann surface with genus $g \geq 2$ has at most $84(g - 1)$ automorphisms. This bound Hurwitz knew to be attained since Klein had exhibited a surface of genus $g = 3$ which admitted PSL(2, 7) as the group of automorphisms. As a result such groups are called now *Hurwitz groups*.

There was not much movement in this area between the begining of the century and 1961 when Macbeath [13], proved that there are infinitely many g for which the Hurwitz bound is attained as well as infinitely many g for which it is not. All that Macbeath needed was a single Riemann surface with a Hurwitz group and for this used the above mentioned Riemann surface (that corresponds to a famous Klein quartic). Then lifting the group of automorphisms to the universal covering obtained an extension of the fundamental group of the surface. Collapsing then the fundamental group to the first homology modulo m, which involves factoring out a normal subgroup of finite index, obtained a finite extension of the orginal group and a finite sheeted covering space of the orginal Riemann surface.

In other words. If X is a Riemann surface of genus $g \geq 2$ with the group G of automorphisms of order $84(g - 1)$ then $G = \Lambda/\Gamma$, where Λ is a triangle group (2, 3, 7) whilst Γ is a surface group of genus g, which turns out to be a fundamental group of X. Collapsing now X to the first homology modulo m, what is the same as factoring out the fundamental group Γ of X by the subgroup Γ_1^m of Γ generated by all commutators and all m-powers we obtain an abelian group of order m^{2g}. Thus we have a surface subgroup Γ_1^m of Γ with index m^{2g}, characteristic in Γ and hence normal in Λ. The corresponding covering space D/Γ_1^m is thus a Riemann surface of genus $g' = m^{2g}(g - 1) + 1$ having $84(g' - 1)$ automorphisms. We have presented this construction because it and its various modifications turns out to be very fruitful and were used latter in numerousous papers. This result has been obtained independently by Lechner and Newman [12], and generalized by Sigerman [17] who showed that if an orientable Riemann surface of genus g having $84(g - 1)$ automorphisms happens to be a two sheeted covering of a non-orientable Riemann surface having maximal group of automorphisms then for given positive integer m there is an orientable Riemann surface of genus $g' = m^g(g - 1) + 1$ which admits $84(g' - 1)$ automorphisms.

Then Macbeath [14] established necesary and sufficient condition for a two dimensional fractional linear group to be a Hurwitz group.

Conder [5] showed that all but 64 alternating groups are Hurwitz groups, and it turns out that there is no shortage of Hurwitz groups, even of given order. J. Cohen [4] investigating extensions of the simple Hurwitz group PSL(2, 7), by abelian gruops established that for any positive integer n there is a positive integer k such that there are at least n non-isomorphic Hurwitz groups of order k.

Finally Conder [6] have investigated all Hurwitz groups of order les than 10^6 showing that there are 32 integers g in the range $1 < g < 11905$ for which there exists a compact Riemann surface with a Hurwitz group of automorphisms.

4. CYCLIC AND ABELIAN GROUPS OF AUTOMORPHISMS OF COMPACT RIEMANN SURFACES

Having a cyclic group G of order N one can ask for a minimum value of $g \geq 2$ for which a Riemann surface of genus g admitting G as a group of automorphisms exists. This problem has been considered by Harvey [10] who found an explicite formula for g in question. Using this formula it was then easy to obtain the Wiman bound $2(2g + 1)$ for the order of a cyclic group of automorphisms of compact

Riemann surface of genus $g \geq 2$. There is however a simple, direct way to establish it and we are going to present it now.

Assume thus that a Fuchsian group Λ, with signature (2.2) admits a normal surface subgroup Γ of genus g with factor being a cyclic group Z_N, where $N \geq 10$, and let θ be the corresponding homomorphism. We are going to show that $\mu(\Lambda) \leq \pi(N - 6)/N$).

Clearly we can assume that $m_1 \leq m_2 \leq \cdots \leq m_r$. If $g > 2$ then $\mu(\Lambda) \geq 4\pi$. If $g = 1$ then $r \geq 0$ otherwise $\mu(\Lambda) = 0$, but then $\mu(\Lambda) \geq \pi$. Hence we can assume that $g = 0$.

If $r \geq 5$ then $\mu(\Lambda) \geq \pi$. If $r = 4$ then the only NEC-groups with the area $\leq \pi$ are those with signatures $(2, 2, 2, k)$ $(k \geq 3)$ and $(2, 2, 3, l)$ $(3 \leq l \leq 5)$. But it is easy to see that none of this groups admit abelian group of order ≥ 10 as a surface kernel factor.

So let Λ be a triangle group (k, l, m). Without loss of generality we can assume that $k \leq l \leq m$. First note that both k and l divide m, otherwise an element of finite order would belongs to Kerθ. Moreover $m = N$, since Z_N has order equal to l.c.m. (k, l, m). In particular $l \geq N/k$. Consequently.

$$\mu(k, l, m) \geq \mu(k, N/k, N) = 2\pi\left(\frac{k-1}{k} - \frac{k+1}{N}\right)$$

It is easy to check that the last value is $< \pi(N - 6)/N$ if and only if $N < 2k$. But then $N = k$ and so $\mu(m, k, l) = \pi(2N - 6)/N > \pi(N - 6)/N$. Consequently by the Hurwitz Riemann formula $N = 4\pi(g - 1)/\mu(\Lambda) \leq 4N(g - 1)/(N - 6)$. Hence $N \leq 2(2g + 1)$.

For any $g \geq 2$ the group $Z_{2(2g+1)}$ can be represented as a surface-kernel factor group of a triangle group $(2, 2, g + 1, 2(2g + 1)$. Summing up

A cyclic group of automorphisms of a compact Riemann surface of genus g has no more than $2(2g + 1)$ *elements. Moreover this bound is attained for every value of g.*

Looking for a bound for the order of an abelian group of automorphisms of a surface of genus g in the Hurwitz form i.e. $q(g - 1)$ one can eaisly see that $q = 12$ and this bound is attained for $g = 2$ (the group $A = Z_2 \oplus Z_6$ acts as a group of automorphisms on a surface of genus $g = 2$). But at the same time this value is the only one for which this is so. Note however that for $g = 2$, $12(g - 1) = 4(g + 1)$. What we are going to show now is that $4(g + 1) = 2(2g + 2)$ (compare with the Wiman bound) is the bound for the order of an abelian group of automorphisms of a compact Riemann surface of genus g.

First we are going to show that for an abelian group A of order ≥ 12 and a Fuchsian group Λ with signature (2.2) admitting A as a surface-kernel factor

$$\mu(\Lambda) \geq \pi(N - 8)/N. \tag{4.1}$$

Assume first $|A| \geq 15$. As in the case of cyclic groups we prove this formula in case $g \neq 0$ or $r \geq 4$. So let $g = 0$ and $r = 3$. Clearly we can assume that Λ has signature (k, l, m), where $k \leq l \leq m$. It is also clear that N divides both kl and km. Hence $N/k \leq l$ and $N/k \leq m$. In consequence

$$\mu(\Lambda) \geq \mu(k, N/k, N/k) = 2\pi\left(\frac{k-1}{k} - \frac{2k}{N}\right)$$

Now the last value is strictly smaler than $\pi(N - 8)/N$ if and only if $N < 4k$. Thus if $N \geq 4k$ then (4.1) holds. If $N = k$, $N = 2k$ or $N = 3k$ and $k \leq 5$ then $N \leq 15$ whilst if $k > 5$, $\mu(\Lambda) \geq \mu(k, k, k) = 2\pi(k - 3)/k \geq \pi$.

For $N = 13$, 14, and 15 A is a cyclic group while the reminding case $N = 12$ is obvious. This verifies (4.1) for every $N \geq 12$.

Now if A is an abelian group of order N acting as a group of automorphisms on a compact Riemann surface of genus g, then $A = \Lambda/\Gamma$, where Λ is a Fuchsian group and Γ is a surface group of genus g. By the Hurwitz Riemann formula and (4.1) we obtain that $N \leq 4N(g - 1)/(N - 8)$. So $N \leq 4(g - 1) + 8 = 2(2g + 2)$. Moreover for any positive integer g the group $Z_2 \oplus Z_{2g+2}$ can be represented as a surface-kernel factor group of a triangle group $(2, 2g + 2, 2g + 2)$. Summing up

An abelian group of automorphisms of a compact Riemann surface of genus g has no more than $2(2g + 2)$ *elements. Moreover this bound is attained for every postive ineger* $g \geq 2$.

As was remarked in [16] this result can be proved as a corollary of another result of Maclachlan. We are indebted a J. J. Etayo Gordejuela for bringing this fact to our knoweledge.

5. SOLUBLE GROUPS OF AUTOMORPHISMS OF COMPACT RIEMANN SURFACES

A triangle group (2,3,7) as perfect group does not admit soluble surface-kernel factors. Thus the Hurwitz bound $84(g - 1)$ is not attained for this class of groups. As a result a soluble group of automorphisms of a compact Riemann surface of genus ≥ 2 has no more than $48(g - 1)$ elements. Chetiya [1] (see also [2]) has shown that

Given a positive integer n there exists a Riemann surface of genus $g = 2n^6 + 1$ *which admits a soluble group of automorphisms of order* $48(g - 1) = 96n^6$.

In fact it is easy to check that for a triangle group $\Gamma = (2, 3, 8)$

$$\begin{array}{ll} \Gamma/\Gamma' \cong Z_2 & \Gamma' = (3, 3, 4) \\ \Gamma'/\Gamma'' \cong Z_3 & \Gamma'' = (4, 4, 4) \\ \Gamma''/\Gamma''' \cong Z_4 \oplus Z_4 & \Gamma''' = (3; -). \end{array}$$

As a result Γ/Γ''' is a soluble group of order 96 acting as a group of automorphisms on a compact Riemann surface of genus $g = 3$. Now aplying the construction of Macbeath mentioned in section 3 Chetiya obtained the result in question.

We are going to present another infinite series of g for which a bound $48(g - 1)$ is attained for soluble groups.

Example. Let $G = Gl(2, 3)$ be the general lineal group of degree 2 over the Galois field $GF(3)$. Then

(i) $|G| = 48$,

(ii) G is soluble and it is easy to check that

(iii) $A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $B = \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix}$ is a pair of generators of order 2 and 3 respectively whose product has order 8.

Thus G acts as a group of automorphisms on a compact Riemann surface of genus $g = 2$. Aplying Macbeath construction we obtain

For a given positive integer n there exists a Riemann surface of genus $g = n^4 + 1$ *that admits a soluble group of automorphisms of order* $48(g - 1) = 48n^4$.

6. NILPOTENT AND *P*-GROUPS OF AUTOMORPHISMS OF COMPACT RIEMANN SURFACES

Let G be a finite nilpotent surface-kernel factor group of a Fuchsian group Λ with signature (2.2). Without loss of generality we can assume that $2 \leq m_1 \leq \cdots \leq m_r$. Zomorrodian [19] has shown that $\mu(\Lambda) \geq \pi/4$. In fact if $g \geq 2$ then $\mu(\Lambda) \geq 4\pi$ whilst if $g = 1$ then $r \geq 1$, otherwise $\mu(\Lambda) = 0$, and in consequence $\mu(\Lambda) \geq \pi$. As a result we have to deal with the case $g = 0$ only.

If $r > 4$ the $\mu(\Lambda) \geq \pi$, if $r = 4$ then then $m_4 \geq 3$, otherwise $\mu(\Lambda) = 0$, and thus $\mu(\Lambda) \geq \pi/3$. Hence we can assume that $g = 0$ and $r = 3$.

If $m_1 \geq 4$ then $\mu(\Lambda) \geq \pi/2$, if $m_1 = 3$ then 3 divides m_2, otherwise G would be cyclic group. If $m_2 = 3$ then since a finite nilpotent group is a direct product of its Sylow p-subgroups, $m_3 = 3^k$, where $k \geq 2$. Thus $\mu(\Lambda) \geq 4\pi/9$. If $m_2 = \alpha 3$ $(\alpha \geq 2)$ then $\mu(\Lambda) \geq 2\pi/3$. Finally if $m_1 = 2$ then arguing as in the case $m_1 = 3$ we have that 2 divides m_2. If $m_2 = 2$ then $\mu(\Lambda) < 0$, whilst if $m_2 \geq 6$ then $\mu(\Lambda) \geq \pi/3$. Thus $m_1 = 2$, $m_2 = 4$ and consequently $m_3 = 2^\beta$. If $\beta > 3$ then $\mu(\Lambda) > 3\pi/8$, while if $\beta = 2$, $\mu(\Lambda) = 0$. Hence $\beta = 3$ and in this case $\mu(\Lambda) = \pi/4$.

(What we have presented above is esentially the Zomorrodian aproach, note however that we have not used the notion of p-localization for signatures of Fuchsian groups what is evidently a too heavy and not necessary tool to deal with triangle groups). As a result Zomorrodian obtained that

A nilpotent group of automorphisms of a compact Riemann surface of genus $g \geq 2$ *has no* more than $16(g - 1)$ *elements. Moreover the bound can be atained only for a 2-group.*

Now it is easy to see that $(a, b | a^2, b^8, abab^5)$ presents a group G of order 16. Thus the bound $16(g - 1)$ is attained for $g = 2$. Iterating Macbeath construction for $m = 2$ one can produce an infinite series of 2-groups that acts as a maximal nilpotent groups on compact Riemann surfaces. Moreover each of this group $\tilde{G}$ is an extension of a factor group H of $\Gamma = (2, -)$ by the group G. This led Zomorrodian to lift a subgroup K of H to a normal subgroup Γ_1 of $\Lambda = (2, 4, 8)$ contained in Γ, in such a way that $\tilde{G}/K \cong \Lambda/\Gamma_1$. Thus using the fact that a 2-group has a normal series with cyclic factors of order 2 Zomorrodian deduces that

Given an integer $n \geq 0$ *there exists a Riemann surface af genus* $g = 2^n + 1$ *that admits a group of order* 2^{n+4} *as a group of automorphisms.*

Maximal nilpotent groups of automorphisms of compact Riemann surfaces turns out to be 2-groups. This led Zomorrodian to consider the analogous problem of finding a bound for the order of a p-group of automorphisms of a compact Riemann surface. Using considerations similar to the preceding ones it is very easy to obtain his main results [20].

A p-group automorphisms of a compact Riemann surface of genus $g \geq 2$ *has at most*

$$\begin{array}{ll} 9(g-1) & \text{if } p = 3, \\ 2p(g-1)/(p-3) & \text{if } p \geq 5, \end{array}$$

elements.

Moreover if $g - 1 = 3^n$, *where* $n \geq 2$, *or* $g - 1 = (p - 3)p^n/2$, *where* $p \geq 5, n \geq 0$ *then there is a surface of genus g that admits a group of order* 3^{n+2}, *and* p^{n+1} *respectively as a group of automorphisms.*

7. METABELIAN GROUPS OF AUTOMORPHISMS OF COMPACT RIEMANN SURFACES

A finite group is metabelian if and only if its commutator is an abelian group. Thus a necessary condition for a Fuchsian group Λ to admit a metabelian group as a surface-kernel factor is that Λ' satisfies Maclachlan l.m.c. condition [14]. Using this simple observation Chetiya and Patra [3] has recently shown that triangle groups (3, 3, 4), (2, 5, 5) and (2, 4, 8) with areas $\pi/6$, $\pi/5$ and $\pi/4$ respectively are the ones with minimal areas that admits finite metabelian surface-kernel factor groups.

It is easy to see that the group (3, 3, 4) admits only one such a factor (a group of order 48). More difficult is the proof that (2, 5, 5) admits only one metabelian surface-kernel factor (a group of order 80). As a result

The bounds $24(g - 1)$ *and* $20(g - 1)$ *corresponding to the groups* (3, 3, 4) *and* (2, 5, 5) *respectively are atained for metabelian groups for the single values of* $g = 3$ and $g = 5$ *respectively only.*

The bound $16(g - 1)$ turns out to be the first that is attained for infinitely many values of g.

Le G be the surface-kernel factor group of a triangle group $\Lambda = (2, 4, 8)$ of order 16 considered in the the previous section, and let $G = \Lambda/\Gamma$, where Γ is a surface group of genus $g = 2$. It is clear that G is metabelian, and thus the second derived group Λ'' of Λ is contained in Γ. Now for an integer n let Γ_n be a group generated by n-powers and commutators of Γ and elements of Λ''. It is clear that each Γ_n is a charactersistic in Γ and hence normal in the whole group Λ. Moreover $[\Gamma : \Gamma_n] = n^{2g} = n^4$. In this way Chetiya and Patra obtain their main result

Given a positive integer n there is a compact Riemann surface of genus $g = n^4 + 1$ *that admits a metabelian group of automorphisms of order* $16(g - 1) = 16n^4$.

Example. It is easy to see that the Hall Senior [8] group $\Gamma_3 e$ is a surface-kernel factor group of (2, 4, 8) of order 32. Also $(\Gamma_3 e)' = Z_4$. As a result we have a metabelian group of order 32 that acts as a group of automorphisms on a compact Riemann surface of genus $g = 3$.

Thus a Chetiya and Patra modification of Macbeath construction mentioned in section 3 led us to deduce that

Given a positive integer n there is a compact Riemann surface of genus $g = 2n^6 + 1$ *with metabelian group of automorphisms of order* $32n^6$.

8. MORE ON SOLUBLE GROUPS OF AUTOMORPHISMS OF COMPACT RIEMANN SURFACE

A soluble group G is said to have degree n or to be n-soluble if n is the the smallest integer such that the n-th derived group $G^{(n)}$ of G vanishes. Thus we can look on abelian and metabelian groups considered before as on 1 and 2-soluble groups respectively. On the other hand it is obvious that all groups of order > 96 considered by Chetiya and described in the section 4 have degree 4. The group of order 96 is the only known 3-soluble group of automorphisms of compact Riemann surface of genus g, that has $48(g - 1)$ elements. We have shown recently [8] that

A 3-*soluble group of automorphisms of a compact Riemann surface of genus* $g \neq 3$, 5, 6, 10 *has order* $\leq 24(g - 1)$. *Moreover given positive integer n there exist a surface of genus* $g = n^4 + 1$ *that admits a 3-soluble group of automorphisms of order* $24(g - 1)$. *A surface of specified above genus may admit bigger* 3-*soluble group of automorphism: of order* $48(g - 1)$ for $g = 3$, $40(g - 1)$ *for* $g = 5$, $36(g - 1)$ *for* $g = 10$, *and* $30(g - 1)$ *for* $g = 6$.

9. SUPERSOLUBLE GROUPS OF AUTOMORPHISMS OF COMPACT RIEMANN SURFACES

Using considerations similar to the preceding ones we have proved recently [7] that Fuchsian groups (2, 4, 6) and (2, 3, 18) with areas $\pi/6$ and $2\pi/9$ respectively are the onces with smalest areas that admit supersoluble surface-kernel factors.

Then we showed that the group (2, 4, 6) admits only one such a factor (a semidirect product of the cyclic group of order 3 and the dihedral group of order 8). As a result

The bound $24(g - 1)$ *corresponding to the group* (2, 4, 6) *is attained for metabelian groups for a single value of* $g = 2$ *only, whilst a supersoluble group of automorphisms of a compact Riemann surface of genus* $g \geq 3$ *has no more than* $18(g - 1)$ *elements.*

Moreover we proved that

A necessary and sufficient condition for a Riemann surface of genus g to admit a supersoluble group of automorphisms of order $18(g - 1)$ *is that* 3^2 divides $g - 1$ *and the only other prime divisors of it are those that are congruent to* 1 *modulo* 3.

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*Oligomerización catalítica de metano sobre óxidos metálicos**

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La oxidación parcial de metano para formar hidrocarburos de cadena más larga, preferentemente C_2, es un proceso de gran relevancia tecnológica y económica en el desarrollo de nuevas alternativas químicas para el uso del gas natural. Dentro de esta línea se han publicado muy recientemente bastantes trabajos en los que se utilizaron catalizadores muy variados. Por ejemplo, Ito et al. [1] encontraron que el MgO dopado con litio es un catalizador activo y selectivo para esta reacción, al mismo tiempo que propusieron un mecanismo donde las especies $Li^+—O^-$ son responsables de la formación de especies radicales $CH_3^{\cdot}$, que se recombinan entre sí mayoritariamente en la fase gaseosa [1,2]. Los óxidos lantánidos se han mostrado también activos en la reacción de oligomerización [3], pero los sistemas catalíticos más ampliamente utilizados son, sin lugar a duda, los óxidos metálicos reducibles [4,5], en los cuales el oxígeno de red es el responsable de la eliminación de un átomo de hidrógeno. Esta última alternativa es explorada en esta comunicación.

Se preparó un conjunto de óxidos metálicos de características básicas, tales como óxidos de Ce, Th, Pr, Sm, Mn, Bi y Sn, soportados sobre α-Al_2O_3 (T-708, Girdler Südchemie). Se utilizó el método de mojado incipiente con disoluciones acuosas de los respectivos nitratos o haluros. Los precursores impregnados se secaron a 120 °C y se calcinaron a 800 °C durante 3 horas. El contenido metálico fue en todos los casos del 5 por 100 en peso. Además de esta serie se preparó otra más incorporando Na como promotor. Para ello, una parte alicuota de cada preparación se reimpregnó con una disolución de nitrato de Na, de concentración adecuada para obtener una carga del 0,2 por 100 en peso. El secado y la calcinación se realizaron en las mismas condiciones que en los precursores no promovidos. La dispersión relativa del metal y del promotor se siguió mediante las técnicas de difracción de rayos X (XRD) y la expectroscopía fotoelectrónica de emisión (XPS). La actividad catalítica se determinó en sistema dinámico en un reactor de lecho fijo a 750 °C para las relaciones molares CH_4:O_2 = 10:1 y 20:1, utilizando la cromotografía gaseosa como técnica analítica.

Se estudió la oxidación parcial de CH_4 tanto sobre los catalizadores no dopados como sobre aquellos dopados con un 0,2 por 100 de sodio. En todos los ensayos se detectaron hidrocarburos C_2^+ (C_2H_6 + C_2H_6) de oxidación parcial y CO_2 de combustión completa. En general, los dos tipos de catalizadores mostraron una gran estabilidad térmica y química, no observándose desactivación aparente a lo largo del ensayo catalítico. Los valores de conversión de CH_4 (%) y de selectividad porcentual a los productos C_2H_6, C_2H_4 y CO_2 a la temperatura de reacción 750 °C para una

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relación molar CH_4/O_2 = 20 y un tiempo de residencia en el reactor de 3,0 g.s/mol se representan por medio de un diagrama de barras en la figura 1. Se realizaron también medidas de actividad para una relación molar CH_4/O_2 = 10, manteniendo constantes los demás parámetros de reacción. En este último caso, la conversión de CH_4 aumentó ligeramente al mismo tiempo que la selectividad total a hidrocarburos C_2^+ disminuyó sensiblemente.

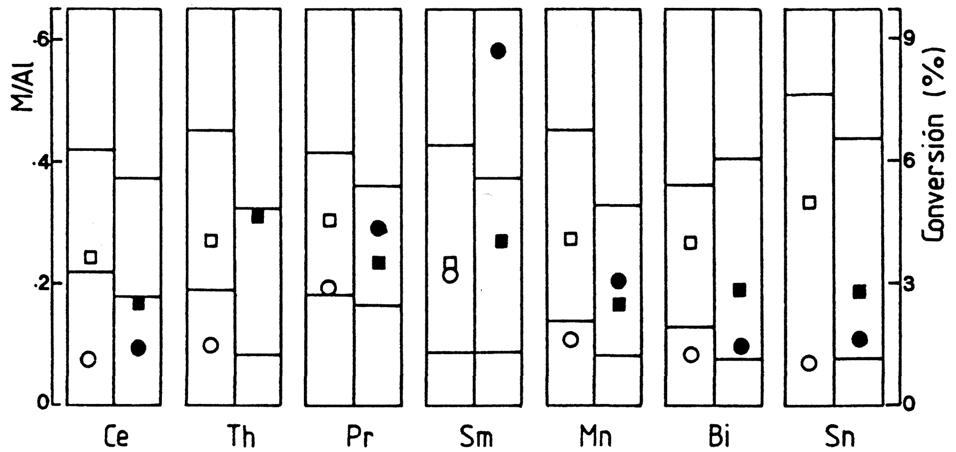

Fig. 1. Conversión de CH_4 (%) para los catalizadores MO_x/Al_2O_3 no promovidos (■) y promovidos con Na (□), a 750 °C, tiempo de contacto W/F = 3 g s/ml y relación molar CH_4/O_2 = 20. La parte superior de cada barra corresponde a la selectividad porcentual a CO_2, la inferior a C_2H_6 y la intermedia a C_2H_4. Se incluyen también las relaciones atómicas superficiales calculadas por XPS para los catalizadores M/Al no promovidos (●) y promovidos con Na (○).

Cuando se comparan los datos de actividad y selectividad de las dos series de catalizadores resulta evidente que el Na presente, probablemente como Na_2O, ejerce, en general, un papel promotor importante. Los catalizadores ThO_2 y Sm_2O_3 son las excepciones, resultando incluso más activos que sus homólogos dopados con Na. Debe tenerse en cuenta que los óxidos de Th y Sm son los más básicos de toda la serie de óxidos empleados en este estudio. Por tratarse de óxidos metálicos soportados, para racionalizar estos resultados se ha medido la relación atómica superficial M/Al, donde M es el catión del óxido MO_x y Al es el aluminio del soporte. Esta relación representa, por tanto, una medida del grado de dispersión del oxido soportado sobre α-Al_2O_3. Como se puede observar en la propia figura 1, las relaciones atómicas M/Al indican en primera instancia que la actividad en la reacción de oligomerización de CH_4 no puede explicarse solamente en términos de dispersión. La naturaleza del oxígeno de red del óxido metálico es otro factor decisivo que debe ser considerado. Mientras que en los óxidos reducibles (Mn_2O_3, Bi_2O_3, SnO_2, Pr_6O_{11} y parcialmente el CeO_2) las especies O^{2-} de red son activas en la oxidación selectiva del CH_4, en los óxidos no reducibles (ThO_2 y Sm_2O_3) son las propiedades ácido-base de los centros M-O^- las que determinan la capacidad del sólido para eliminar un átomo de hidrógeno de la molécula CH_4.

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