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Catalytic dehydrogenation of propane over cluster-derived Ir–Sn/SiO_2 catalysts

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The dehydrogenation of propane was studied in gas-phase at 773 K over two series of silica-deposited Ir–Sn systems: the bimetallic catalysts obtained from Ir–Sn carbonyl clusters precursors and the ones prepared by deposition of a metallorganic Sn precursor onto preformed Ir nanoparticles. In the comparison, cluster-derived catalysts showed good propane conversion, optimal selectivity to propene and high stability under the severe reaction conditions.

KEY WORDS: propane dehydrogenation; bimetallic catalysts; iridium–tin; cluster-derived catalysts; gas-phase.

1. Introduction

Multicomponent catalysts have recently found widespread use, as the combination of two or more metals can lead to synergistic effects such as increased activity, enhanced catalyst lifetime and improved product selectivity [1–3]. In particular, supported bimetallic catalysts have shown interesting properties for many reactions, such as hydrogenation of alkynes and dienes in olefine feedstock [4], selective hydrogenation of unsaturated aldehydes [5], preferential oxidation of CO [6] or dehydrogenation of light alkanes [7]. The changes in catalytic properties are attributed to a decrease in the number of contiguous active sites (''ensemble effect'') as well as to changes in the electronic nature of the active metal particles (''electronic effect''). In fact, by adding a second component to a noble metal-based catalytic system, it is possible to modify in different ways the catalytic behaviour in structure sensitive reactions, which require a defined number of contiguous active sites (e.g. cleavage or formation of C–C bonds) or structure insensitive reactions (e.g. cleavage or formation of C–H bonds), which do not need it. The relative importance of the two effects could be therefore evaluated by studying systems over which both structure sensitive and structure insensitive reactions are carried out at the same time.

In the metal-catalysed transformation of light alkanes, the hydrogenolysis is considered as a structure-sensitive reaction as it takes place over an ensemble of adjacent atoms, whereas the dehydrogenation is a structure-insensitive process [8–15]. In this field, some studies were carried out on Pt–Sn-based catalysts [16–22], while very little work has been performed on the closely related system, Ir–Sn. In addition, some of the few literature reports about the catalytic application of Ir–Sn system were obtained on catalysts with a high content (up to 10 wt%) of noble metal [19, 23, 24]. However, a NaY–zeolite-supported Ir–Sn catalytic system with a low Ir loading (1 wt% Ir) revealed high selectivity for the dehydrogenation of propane to propene at 773 K (>95% at 20% conversion) and, in presence of hydrogen, maintained thermodynamic conversion levels for up to 24 h [24]. Such remarkable performances were ascribed to the synergy of two effects: the electronic modification and the covering of the iridium due to the presence of tin. But tin might also play a role in enhancing the surface removal of hydrogen, hence leading to a more marked dehydrogenating activity [13].

The requirement of having definite composition, uniform size and shape is particularly difficult to achieve in the case of well-dispersed bimetallic nanoparticles.

In the present work, the reactivity of monometallic iridium catalyst was compared with that of bimetallic Ir–Sn systems, obtained from different metal precursors, in the propane dehydrogenation, to have a deeper insight into the influence of tin on iridium. Indeed, the aim is to investigate if and how the deposition of specifically designed large molecular metal clusters (with cores of four or six iridium atoms [20]) with pre-formed Ir–Sn bonds onto silica supports can lead to the preparation of catalysts with a more defined chemical environment and with enhanced performances. In addition, by using two silica materials with different specific surface areas and morphologies, it is possible to study the

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influence, if any, of the structural features of the support on the size and dispersion of the nanoparticles and catalytic performances.

2. Experimental

2.1. Catalysts preparation

Two mesoporous silica materials were used as supports: a non-ordered commercial silica purchased from Grace (from now onwards SiO_2; mean pore diameter, total porous volume and specific surface area, 20.4 nm, 1.48 $cm^3\ g^{-1}$ and 290 $m^2\ g^{-1}$, respectively) and an ordered purely siliceous MCM-41 (mean pore diameter, total porous volume and specific surface area 2.8 nm, 1.36 $cm^3\ g^{-1}$ and 1024 $m^2\ g^{-1}$, respectively). SiO_2 was stirred for 5 h in 1 M HNO_3 and then washed with high-purity deionised water (MilliQ) to neutrality before use. MCM-41 was synthesized with pores wall of about 2 nm according to the procedure described in literature [26].

Two main synthetic ways were followed to obtain the catalysts: a ''single source'' and a ''dual source'' method.

Single source precursors were either $[N(C_2H_5)_4]_2[Ir_4(CO)_{10}(SnCl_3)_2]$ or $[N(C_2H_5)_4][Ir_6(CO)_{15}(SnCl_3)]$ metall-organic clusters, prepared as described elsewhere [25]. Before impregnation, the non-ordered silica was treated at 773 K in air for 5 h and *in vacuo* overnight, stirred in MilliQ water for 4 h, dried and then treated at 573 K in air for 5 h and *in vacuo* overnight. Similarly, MCM-41 was treated at 573 K in air and then left *in vacuo* overnight. Impregnation occurred via anhydrous CH_2Cl_2 (Fluka) solution of the cluster precursor. The suspension was stirred for 12 h under Ar and the solvent was then removed under vacuum in the case of Grace SiO_2, whereas via filtration under Ar atmosphere for MCM-41.

According dual source path, iridium nanoparticles were first prepared by impregnating the supports with a solution of $IrCl_3{\cdot}3H_2O$ (Engelhardt) in hydrochloric acid aqueous (typically 1.5 mL of 36% HCl in 60 mL of MilliQ water). After drying, the iridium-containing samples were calcined for 1 h under oxygen flow (100 mL min^{-1}; 573 K) and then reduced for 1 h under hydrogen flow (100 mL min^{-1}; 643 K). Then tin was deposed via evaporation of a solution of $Sn(n\text{-}C_4H_9)_4$ (Aldrich, 93%) in anhydrous toluene (Riedel de Haen).

All catalysts were stored under Ar atmosphere prior to use. The metal contents of the prepared catalysts are summarised in table 1.

2.2. HR-TEM characterization

The reduced samples and the used samples after catalytic tests have been grinded and the powder ultrasound dispersed in *iso*-propanol for high-resolution transmission electron microscopy (HR-TEM) analysis. A drop of the suspension has been deposited on the carbon grid which, after solvent evaporation under vacuum, has been inserted in the column of the JEOL Jem-2010 EX high resolution transmission electron microscope. The instrument is equipped with an energy dispersive X-ray spectrometer (EDX; minimum probe spot 5 nm). EDX signals of Ir and Sn (L line area) measured at different points were rationed with respect to the levels of Si (K line area), taken as internal reference and equally distributed in the material. Due to the absence of calibration, the obtained values provide only qualitative estimations of the metal contents (moreover, a metal loading of about 1 wt% or lower, corresponds to molar fraction of Ir and Sn at the limit of the sensitivity of the EDX probe, even when single metal particles are selected). Pictures have been taken at 300K–800K magnifications, spanning wide regions of several support grains in order to provide a well representative map of the catalyst. Distribution histograms of metal particles diameters, evaluated from about 250 to 450 counts per sample, exhibit peaks centred on the reported mean values, together with the corresponding standard deviations.

2.3. Catalytic studies

All samples were *in situ* reduced for 1 h at 773 K under hydrogen (50 mL min^{-1}) just before catalytic tests and reaction mixture admission. The reaction was carried out in a fixed-bed continuous-flow glass reactor (typical powder load = 150 mg) at 773 K at atmospheric pressure with a propane/hydrogen/helium feed (1 : 1 : 8 molar ratio) such as to obtain a space velocity of ca. 0.2 (mol C_3H_8) (mol Ir)$^{-1}$ s^{-1}. The addition of a small fraction of hydrogen in the feed helped to maintain a stable activity of the catalysts during the tests [7]. Quantitative analysis was performed with an on-line GC-FID instrumentation (Carlo Erba HRGC 4960) equipped with a Poraplot Q column (0.53 mm i.d.; 25 m length). The catalytic system reached steady conversion and selectivity values in about 3 h. After that stabilisation period, activity and selectivity were very stable and, in the present work, they are reported after 24 h on stream. The amount of carbon on the catalysts before and after catalytic runs was evaluated by CHN elemental analysis. In order to exclude any catalytic activity of the support, both MCM-41 and Grace silica materials alone were tested in catalysis and no propane conversion was detected.

3. Results

3.1. Catalysts preparation

In the catalysts derived from ''single source'' precursor, both iridium and tin are added at the same time in one step. In this case, the systems are obtained from Ir–Sn carbonyl clusters, in which the intimate atomic contact and the desired Sn/Ir atomic ratio is already present in the starting precursor.

Table 1
Composition of the catalysts

Catalyst	Precursor	Ir content (wt%)[a]	Sn content (wt%)[a]
Ir/SiO_2	$IrCl_3$	0.86	–
$Ir_{5.9}+Sn_1/SiO_2$	$IrCl_3+Sn(n\text{-}Bu)_4$	0.78	0.08
$Ir_{1.8}+Sn_1/SiO_2$	$IrCl_3+Sn(n\text{-}Bu)_4$	0.78	0.27
$Ir_{1.5}+Sn_1/SiO_2$	$IrCl_3+Sn(n\text{-}Bu)_4$	0.86	0.35
$Ir_{0.8}+Sn_1/SiO_2$	$IrCl_3+Sn(n\text{-}Bu)_4$	0.75	0.59
Ir_4Sn_2/SiO_2	$[N(Et)_4]_2$ $[Ir_4(CO)_{10}(SnCl_3)_2]$	1.02	0.29
Ir/MCM-41	$IrCl_3$	1.28	–
Ir_4Sn_2/MCM-41	$[N(Et)_4]_2$ $[Ir_4(CO)_{10}(SnCl_3)_2]$	0.68	0.22
Ir_6Sn_1/MCM-41	$[N(Et)_4]$ $[Ir_6(CO)_{15}(SnCl_3)]$	0.71	0.11

[a]As obtained from ICP-AES analysis.

Adsorption of $[N(C_2H_5)_4]_2[Ir_4(CO)_{10}(SnCl_3)_2]$ and $[N(C_2H_5)_4][Ir_6(CO)_{15}(SnCl_3)]$ onto MCM-41 caused the support becoming orange within 15 min and the previously orange CH_2Cl_2 solution becoming light yellow. After filtration of the slurry and drying, the samples were homogenously yellow. Stirring the as-synthesised Ir_4Sn_2/MCM-41 sample in CH_2Cl_2 caused no significant changes in colour of either the powder or the solvent. FT-IR analysis of extraction solution revealed no carbonyl Ir species. This means that the cluster is irreversibly chemisorbed onto the MCM-41 surface and it cannot be extracted by using the impregnation solvent. Conversely on SiO_2, the desired amounts of Ir and Sn (ca. 1 and 0.3 wt%, respectively) have been reached only by evaporation of the impregnation solution. In fact, previous attempts in synthesising Ir_4Sn_2/SiO_2 directly by impregnation and filtration of the slurry (as for MCM-41), revealed that only very low metal loadings (ca. 0.3 wt% for Ir and 0.1 wt% for Sn) could be obtained. Actually, SiO_2 possesses a smaller specific surface area than MCM-41 and consequently only lower amounts of cluster precursors can be accommodated and chemisorbed onto its surface. The remaining precursor has to be physisorbed by removing the solvent. Activation of all the cluster-containing silica materials in hydrogen at 773 K led to light grey powders. XRD analysis of the samples before and after reduction revealed no remarkable changes in MCM-41 structure due to adsorption of Ir–Sn cluster. Therefore, neither the impregnation nor the reduction steps affected the ordered network of MCM-41 mesopores.

In the catalysts derived from "dual source" precursors, first iridium is deposited by impregnation from iridium chloride. Then, tin is added in a second step, when the metallic iridium particles are already formed on the silica surface. Such a synthesis methodology in two steps should allow studying the influence of the tin addition onto a catalyst which is already structured and whose catalytic performances are widely known.

During the deposition of $Sn(n\text{-}C_4H_9)_4$ dissolved in toluene solution onto the Ir catalyst, no significant changes in Sn concentration were detected in 24 h by monitoring the solution by GC–MS analysis. So no specific adsorption occurred in this case, whereas tin tetraalkyl precursors are easily adsorbed on Pt based systems [27–28]. Such observation prompted us to deposit tin onto the iridium-containing solid by impregnation of tetrabutyltin solutions in toluene followed by evaporation of the solvent.

3.2. Characterization

The location and the morphology of the metal particles after the catalyst activation under hydrogen were inspected by HR-TEM. The micrographs of the catalysts derived from $IrCl_3$ (namely, Ir/SiO_2, $Ir_{0.8}+Sn_1/SiO_2$, $Ir_{1.8}+Sn_1/SiO_2$ and $Ir_{5.9}+Sn_1/SiO_2$) show that the metal particles are small (in all cases the average value is below 2 nm) and rather uniform in size (table 2 and figure 1a).

The catalysts obtained from single source (namely, Ir_4Sn_2/MCM-41, Ir_6Sn_1/MCM-41 and Ir_4Sn_2/SiO_2 samples) displayed even lower mean particle diameters (1.2 nm on SiO_2 and 1.1 nm on MCM-41) with narrower particle size distribution and no metal aggregates bigger than 2.5 nm were detected (figure 1). The role of the high specific surface area of the silica support is

Table 2
Average size (d) and full-width half-maximum (FWHM) values of Ir–Sn metal particles as obtained by HR-TEM analysis

Sample	d (nm)	FWHM (nm)
Ir/SiO_2	1.61	0.71
$Ir_{0.8}+Sn_1/SiO_2$	1.71	0.55
$Ir_{1.8}+Sn_1/SiO_2$	1.36	0.74
$Ir_{5.9}+Sn_1/SiO_2$	1.79	0.61
Ir_4Sn_2/SiO_2	1.18	0.35
Ir/MCM-41	1.19	0.20
Ir_6Sn_1/MCM-41	1.15	0.26
Ir_4Sn_2/MCM-41	1.09	0.42
Ir_4Sn_2/MCM-41 after catalysis	1.08	0.43

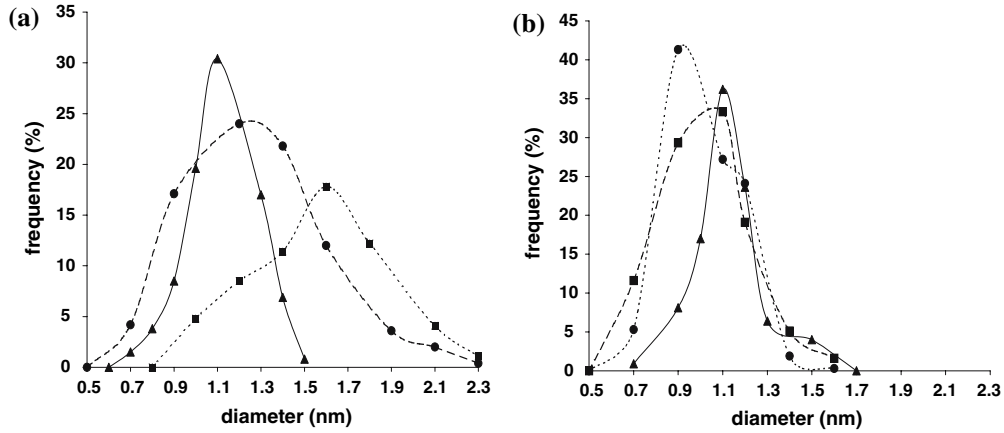

Figure 1. Size distribution of Ir–Sn metal particles as obtained by HR-TEM analysis. Graph A: Ir_4Sn_2/SiO_2 (), Ir/SiO_2 (■), $Ir_{1.8}+Sn_1/SiO_2$ (●). Graph B: Ir_4Sn_2/MCM-41 after catalysis (), Ir_4Sn_2/MCM-41 (■), Ir/MCM-41 (▲;).

evident when Ir_4Sn_2/MCM-41 and Ir_4Sn_2/SiO_2 are compared: over MCM-41 it was possible to obtain metal particles which were smaller in size than those prepared over SiO_2. In addition, it is worth highlighting that cluster-derived systems are also remarkably stable under catalytic conditions. For instance, no change in particle size was recorded in Ir_4Sn_2/MCM-41 after a reaction time of 24 h under the severe conditions here used (figure 1b).

More precise information on the distribution of Ir and Sn over the support crystallites was given by combined TEM/EDX analysis of the samples. As an example, figure 2 reports the results obtained for one section of $Ir_{1.8}+Sn/SiO_2$ and Ir_4Sn_2/MCM-41. In the former catalyst, amorphous silica grains were observed. Conversely, in the latter one, prismatic MCM-41 crystallites with sizes in the 100–200 nm range with well-formed channels fringes (which disappear for prolonged exposition to the electron beam) were recorded. Small black spots are Ir–Sn particles, while numbers in white circles in the images indicate the points, ca. 50 nm apart, where the EDX analysis was carried out using a spot size of ca. 10 nm and moving the electron beam from the border to the core of the section. In the image inset are reported the EDX signals corresponding to the different points evidenced in the TEM picture. Although this measure provides only a semi-quantitative estimation of the relative concentration of the two metals, the fact that all values are similar in the whole section and the Sn/Ir ratio corresponds fairly well to that in the precursor cluster, indicates that the metals are quite homogeneously distributed in the material. More precisely, slightly lower relative Sn/Ir contents were only detected in proximity of the larger metal particles, suggesting that large particles are richer in Ir than expected from stoichiometric ratio. No more detailed information on the bimetallic relative composition was obtainable due to the fact that the particle size is lower than the EDX probe spot.

3.3. Catalytic studies

The monometallic iridium-based systems showed a high conversion of propane, but a very poor dehydrogenating activity (table 3; entries 1 and 2). Indeed, the use of Ir alone led to the almost complete formation of methane and a negligible production of propene. In addition, the morphology of the siliceous support (i.e. Ir/SiO_2 *vs.* Ir/MCM-41) did not play an essential role, as the selectivity values to propene and methane were fully comparable.

On the other hand, when tin was added into the catalyst by either single or dual source, a sensible reduction of propane conversion was recorded and bimetallic catalysts were up to three times less active than monometallic ones. However, the methodology of tin addition had a major influence on the selectivity of the catalyst. The catalyst obtained by tin deposition from dual source (entry 3) revealed a sensible, even if very moderate, increase in dehydrogenation (propene selectivity turned out to be three times greater than in Ir samples), but hydrogenolysis to methane was still the main reaction. Conversely, the deposition of tin in one step directly from bimetallic clusters led to highly selective dehydrogenating catalysts (entries 4–6). In all cases, propene was the main reaction product and the formation of methane was practically inhibited. Specifically, the samples derived from Ir_4Sn_2 cluster (entry 5), maintained a very high propane conversion, near to the thermodynamic conversion values at 773 K, that is about 22%, under similar reaction conditions [24]. In addition, all the cluster-derived catalysts showed an excellent stability under catalytic conditions: very stable conversion and selectivity values were obtained over Ir_4Sn_2/MCM-41 under working conditions for 24 h. With regard to selectivity, Ir_4Sn_2/MCM-41 displayed the best results, as most of the propane is converted into propene and only tiny amounts of hydrogenolysis

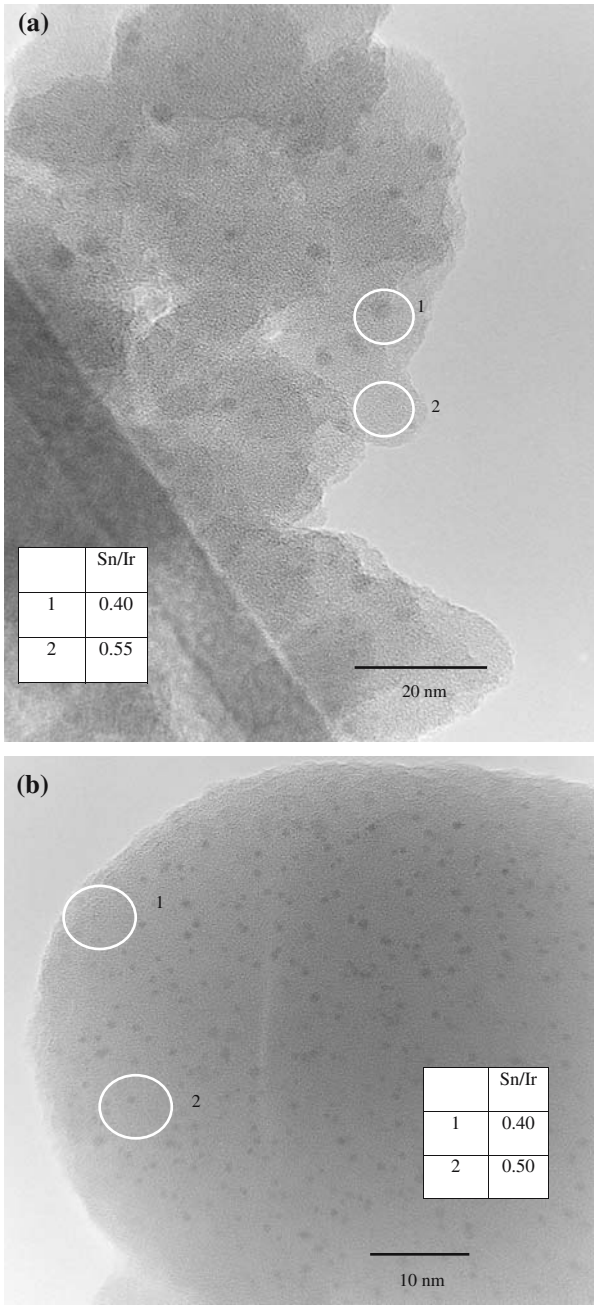

Figure 2. HR-TEM picture of (a) $Ir_{1.8}+Sn_1/SiO_2$ and (b) Ir_4Sn_2/MCM-41. In the inset tables, Sn/Ir relative compositions as detected by EDX analysis (integrated peak area) in the regions marked by white circles.

products were detected. The use of a non-ordered support (SiO_2 versus MCM-41) gives rise to slightly lower conversion and selectivity values. Such a small decrease is likely due to the lower dispersion of the metal particles in SiO_2-based systems than in MCM-41-based ones (table 2) and hence to the relatively lower exposure and accessibility of active sites in the former catalysts.

The use of another cluster with a different metal ratio (Sn/Ir = 0.17; entry 6) led to worse performance, namely lower conversion and lower selectivity. Due to this last result, the attention was then focused on how the molar ratio of the active metal to the promoter could affect the catalytic properties and if it were possible to reproduce the interesting performances obtained over the cluster-derived catalyst by simply changing the promoter to active metal ratio. For this purpose, a series of catalysts with different Sn/Ir ratios was prepared and tested (figure 3). It is evident that, when Sn/Ir is low, the catalyst displays a behaviour similar to pure Ir systems. Nevertheless, when the Sn/Ir ratio reaches the typical value of about 0.6, a drastic loss in conversion is obtained together with a large increase in selectivity to propene. For larger amounts of tin a further increase in propene selectivity was observed, even if with very low conversion values. In summary, in all cases, Ir + Sn catalysts, prepared from dual source, have shown poorer performances with respect to Ir–Sn systems derived from preformed clusters. Hence, a simple variation of the Sn/Ir ratio due to the addition of tin modifier onto pre-formed iridium particles is not enough to obtain efficient dehydrogenation catalysts.

Finally, the content of carbon after a reaction time of 24 h, as obtained from elemental analysis, is listed in table 3. The amount of carbon was higher for the catalysts that showed a good selectivity to propene (entries 4–6), while it was sensibly lower for the systems that led preferentially to the production of methane (entries 1–3). The presence of carbon in the cluster-derived samples is due mainly to carbonaceous deposits formed during the catalytic activity. In fact, the content of carbon in the reduced catalysts, before the catalytic tests, is ca. 0.2 and 0.3 wt%, for Ir_4Sn_2/MCM-41 and Ir_6Sn_1/MCM-41, respectively. The remaining amount of carbon is attributable to aliphatic hydrocarbons formed on the catalyst surface during the reaction, as confirmed by extraction with organic solvent of the spent catalysts and GC-MS analysis of the extraction solution. For $Ir_{1.8}+Sn/SiO_2$, the carbon content before catalysis was higher (ca. 0.6 wt%) and this means that the amount of carbon due to organic deposits produced during the reaction is lower. However, since no loss in catalytic performance was detected during the 24 h of reaction, neither on cluster-derived catalysts nor on solids from double source, the presence of these carbonaceous compounds, whatever their amount, did not lead to any deactivation of the catalysts.

4. Discussion

From the results here reported, it is evident that an intimate contact between iridium and tin sites is essential in order to have not only high selectivity to propene, but also good propane conversion. For this purpose, catalysts derived from single source are the best choice, as the contiguity of Ir and Sn atoms is already present in the starting cluster precursor.

Table 3
Performances of Ir and Ir–Sn systems in the catalytic dehydrogenation of propane after 24 h on stream

Entry	Catalyst[a]	C^b C_3H_8 (% mol)	S^c C_3H_6 (% mol)	S^d CH_4 (% mol)	C content[e] (wt%)
1	Ir/SiO_2	31	2	97	1.1
2	Ir/MCM-41	30	2	97	1.0
3	$Ir_{1.8} + Sn_1/SiO_2$	20	7	92	0.7
4	Ir_4Sn_2/SiO_2	16	88	4	2.9
5	Ir_4Sn_2/MCM-41	18	95	2	2.4
6	Ir_6Sn_1/MCM-41	11	83	10	2.2

[a]Reaction conditions: C_3H_8:H_2:He = 1:1:8; 773 K; space velocity = 0.22 ± 0.03 (mol C_3H_8) (mol Ir)$^{-1}$ s^{-1}; main by-product: ethane.
[b]Propane conversion.
[c]Selectivity to propene.
[d]Selectivity to methane.
[e]Content of carbon after 24 h on stream (from elemental analysis).

Therefore, since the thermal pretreatment under hydrogen does not lead to massive and evident segregation of metallic species, as shown by HR-TEM/EDX analysis, the hydrogenolytic activity of Ir aggregates is depressed by the presence of Sn centres dispersed within (or, at least, in very close contact with) metal particles. So, even though no exact localization of Sn with respect to Ir sites is possible below the 5 nm scale (the threshold dimension of the EDX probe spot), it is possible to affirm that the two metals are in contact at nanometric scale.

The catalytic behaviour recorded over single source catalysts is thus consistent with the observation on related Pt–Sn systems [18], according to which Sn atoms act both as geometrical modifiers, inhibiting the formation of the adjacent-atom aggregates (responsible for hydrogenolysis), and as electronic modifiers, reducing electronic density of the Ir sites. Also in this case, for a thorough estimation of the electronic effect of the Sn sites onto Ir ones, an evaluation of the oxidation states of Sn species could be useful and work is in progress to determine these values.

When the amount of Sn is relatively small in the cluster with respect to the amount of Ir (i.e. Ir_6Sn with respect to Ir_4Sn_2 systems), the geometrical and electronic effects are less marked. In fact, the selectivity to propene decreases and the hydrogenolysis reaction is enhanced.

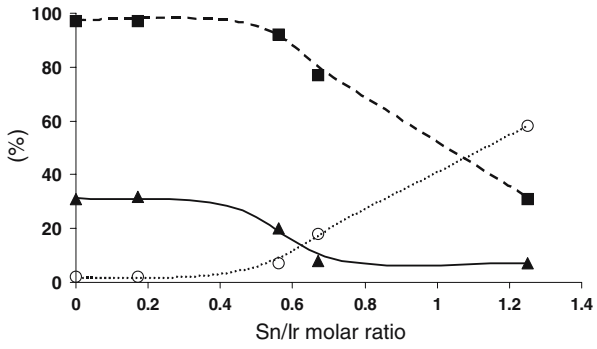

Figure 3. Propane conversion (▲), selectivity to propene (○) and selectivity to methane (■) of Ir + Sn/SiO_2 catalysts with different Sn/Ir molar ratio.

On the other hand, as far as the catalysts derived from dual sources are considered, in no tests the selectivity to propene was as good as the one obtained over cluster-derived systems, whatever the Sn to Ir ratio. More precisely, the maximum selectivity to propene was ca. 60% for $Ir_{0.8} + Sn/SiO_2$ (figure 3), whereas with cluster-derived catalysts by far higher selectivity values (83–95%) were always obtained (table 3; entries 4–6). Actually, on these systems the Ir metallic particles are formed in a previous step. Then, the following addition of Sn gives rise, for low Sn loadings, to a pure-Ir-like behaviour (i.e. good propane conversion, but with formation of methane only), whereas, for higher Sn loadings, to an excessive covering of the Ir sites and to a global decrease in propane conversion.

In this case too, the EDX analysis did not reveal any evident segregation of Ir and Sn species within the range of 5 nm. This means that the Sn species are placed in very close proximity of the Ir atoms (but not in intimate contact as for single source systems) and that a threshold Sn to Ir atom ratio is needed to have a sensible geometrical and/or electronic effect of Sn species onto Ir. Such threshold value is, for the catalysts here considered, around 0.6 (molar ratio). However, too large amounts of Sn atoms lead to the progressive coverage of the Ir metal particles and hence to an inhibition of the catalytic activity. Nonetheless, the performance of $Ir_{0.8} + Sn_1/SiO_2$ suggests that the hydrogenolysis sites are inhibited more easily than the dehydrogenation ones (figure 3).

With regard to the influence of the morphology of the siliceous support, if the cluster precursor is deposited onto a high surface-area silica (Ir_4Sn_2/MCM-41) the formation of well-dispersed ad evenly separated bimetallic particles is optimal and the side formation of methane is practically inhibited. In addition, a complete irreversible chemisorption of the cluster species was possible only over MCM-41 and not over SiO_2, thanks

to the larger availability of surface silanol reacting groups in the former than in the latter. However, the data display that the improvement passing from SiO_2 Grace to MCM-41 is not remarkable and therefore the use of an ordered mesoporous material is not a key issue, at least in this reaction and under these conditions.

5. Conclusions

The catalytic tests, carried out in this work, evidenced that the deposition of bimetallic Ir–Sn clusters on a silica support and its following decomposition under hydrogen is a way to obtain highly selective Ir–Sn active systems for the dehydrogenation of propane at 773 K.

In particular, cluster-derived Ir–Sn systems showed:

- Very high selectivity (ca. 95%) to propene at good values of propane conversion.
- High degree of metallic particle dispersion (mean diameter < 2 nm) with narrow size distributions.
- High stability under catalytic conditions during the reaction time (negligible loss of activity and no agglomeration of the metallic particles).

Furthermore, the use of an ordered mesoporous siliceous support with high surface area, such as MCM-41, allowed an optimal dispersion of the cluster precursor and hence of the metallic particles, generated from the reduction of the cluster metal cores.

A higher degree of metal dispersion and a more homogeneous contact between the iridium and the tin sites were observed with the cluster-derived samples as compared to the dual source prepared ones. Structural characterization of these catalysts by EXAFS and other techniques is in progress and it will be reported separately.

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