PROMOTERS STATE AND CATALYST ACTIVATION DURING AMMONIA SYNTHESIS OVER Ru/C

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ABSTRACT

Carbon-supported, promoted Ru-based catalysts for ammonia synthesis proved to be interesting substitutes for the traditional Fe-based ones. A debate recently arose on the active state of promoters, mainly Cs and Ba, and on the effect of the latter on Ru active sites. In the present work a set of Ba-, Cs- and K-promoted samples has been characterised by various techniques. Higher H_2 and O_2 uptakes have been observed during reduction and chemisorption, respectively, on Cs- and K-promoted samples supported on graphitised carbon. No evidence of this has been observed with samples supported on active carbon. This is in line with the hypothesis of alkaline promoters partial reduction under the ammonia synthesis conditions, favoured by the formation of graphite intercalation compounds. Furthermore, some suggestions are here introduced on the beneficial role of Ba, especially in increasing the support resistance to methanation. Finally, the efficacy of catalyst activation was found to depend on the nature of Ru precursor. Indeed, a prolonged activation at relatively high temperature is usually needed with chloride precursors, to remove the counterion, a poison for the catalyst, whereas less dramatic conditions are required for different precursors, such as nitrosylnitrate.

Keywords: Ammonia synthesis catalyst; Intercalation compounds; Temperature programmed reduction; Alkali metals reduction.

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1 - INTRODUCTION

Ru-based catalysts raised interest in the last years as possible substitutes for the traditional Fe-based ones for the synthesis of ammonia [1-7]. Many possible formulations have been proposed, widely differing as for support (mainly active or graphitised carbon [2,4-6,8] and MgO [9-11]), Ru precursor (chloride [5,12,13], potassium ruthenate [2], carbonyls [14-16], nitrosylnitrate [17,18]) and promoters (alkali-, alkali-earth- and lanthanide-oxides).

In the recent past, a considerable body of papers aimed at throwing light on one of the key factors of this reaction on Ru-based catalysts, *i.e.* its structure sensitivity. It has been proposed that catalyst activity is dominated by Ru step sites, so called B5, whose concentration strongly depends on Ru particle size and hence on metal dispersion. Some work has been carried out both from a more theoretical point of view [8, 19-23] and from a more applicative approach [17].

As for promoters effect, since the earlier work of Aika and co-workers [1,24] it is widely accepted that unpromoted Ru-based samples are almost completely inactive during ammonia synthesis, mainly when active or graphitised carbon is used as support, due to its electron-withdrawing effect [25]. Among the possible promoters, electron-donors are preferred, in order to facilitate electron transfer to Ru and so to enhance the rate of the rate-determining step of the reaction, *i.e.* the dissociative adsorption of N_2 [3,26]. However, more recently the interest was mainly focused on Ba, Cs and K as possible promoters, leading to catalysts which allow overperforming the unpromoted samples, especially when added altogether, so to develop a synergistic effect [13,25].

The active form of Ba seems to be BaO [13,18,27], partly covering the Ru active particles, hence possibly exploiting a structural effect, by modifying the concentration and

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stability of surface sites. This promoter would indeed favour the exposition of crystallographic faces that are active for nitrogen adsorption, so favouring the formation of B5 sites [13,28]. A debate however arose around this hypothesis [18], the formation of B5 sites seeming similar for Ba-promoted and unpromoted samples. In this alternative view Ba was proposed essentially as electronic promoter [18,27].

The role of K and Cs is a bit clearer, their action being essentially of electronic nature. Indeed, alkaline metals play an electron-donor role even in their oxidised form [1] as evidenced by XPS experiments [25]. However, some recent new findings seem to point to the possible partial reduction of Cs and K to metal state during catalyst activation [13,28,29]. A highly reduced state has been so hypothesised (Cs_xO_y), even down to the Cs metallic state.

Another reported difference between the various catalytic systems concerns catalyst activation before reaction, carried out under widely different conditions in order to get optimal catalytic performance. For example, a short activation route has been proposed [2,17], consisting in heating by 1°C/min up to 450°C, then kept for 5 hours, taken as example also by others [5]. By contrast, a much longer activation is reported *e.g.* in [13], consisting in reduction in H_2 at 150°C for 16h, then at 350°C for the same time during catalyst preparation. Then, before reaction, the samples were further reduced in H_2+N_2 for 24 h at 400°C, then for 24 h at either 430°C or at 470°C, depending on the promoter. Furthermore, Hinrichsen *et al.* underlined the need of prolonged activation, so to attain the best catalytic performance [30], addressing short activation as the main cause of less good results.

The following questions can then arise about the effect of sample activation: *i)* can activation be useful for sample conditioning and for the reduction of the layer of passivated Ru only, or does it play a role in Ru redistribution in its active form (*i.e.* does it affect Ru

dispersion)?; *ii*) is catalyst activation able to bring the alkaline promoter(s) to a reduced (metallic) state?; *iii*) what is the role of the carbon support in this scenario?

The goal of the present work was then to answer these questions by investigating a set of unpromoted, singly promoted and multiply promoted Ru/C catalysts, prepared with two different supports, differing for their graphitisation degree. The promoters considered were Cs, Ba and K, used also for the preparation of blank samples (*i.e.* without Ru) for comparison purposes. The samples were characterised by temperature programmed reduction and oxygen chemisorption and by performing many different activation treatments. Some activity tests, carried out after the different activation procedures, completed the present investigation.

2 - EXPERIMENTAL

2.1 - Samples preparation

All the samples were prepared by impregnation from aqueous solutions, using two different supports: a graphitised carbon, referred to as GC, with BET specific surface area (SSA) = 280 m^2/g, and a commercial active carbon, referred to as AC, with SSA = 1400 m^2/g. Ru was deposited from $Ru(NO)(NO_3)_3$ as described in detail elsewhere [17], achieving a final Ru/C loading of 3.8 wt%. The sample was reduced in flowing hydrogen at 320°C for 5 hours. The Ru/GC sample was split into five portions, three of which were impregnated with only one single promoter (Cs, Ba or K) using an aqueous solution of nitrate, the fourth was impregnated with the three promoters altogether and the fifth was left unpromoted. The promoters/Ru atomic ratios, optimised in a previous work [25] were Cs/Ru = 1, Ba/Ru = 0.6, K/Ru = 3,5 (mol/mol). A series of blank samples, *i.e.* without Ru, was also prepared (Table 1). A comparative sample was prepared by impregnation from

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RuCl$_3$·3H$_2$O, reduced under the same conditions and promoted with Ba+Cs+K in the same optimal amount.

2.2 Samples characterisation

SSA was measured by N$_2$ adsorption at 77 K, using a Micromeritics ASAP 2010 apparatus. Temperature programmed reduction (TPR) was carried out by means of a home-made apparatus described in detail elsewhere [31]. The experiment was made on *ca.* 0.15 g of catalyst (0.15-0.25 mm particle size), in 5% H$_2$/Ar gas mixture, by heating (10°C/min) up to different temperatures and for different times, as detailed in Table 2. Samples reduction was followed by flushing in He as reported in the same Table. The total gas flow rate in both cases was 40 cm^3/min. The samples were then cooled to 0°C and several pulses of 10% O$_2$/He mixture were injected, until the peak area of the outcoming oxygen became constant (sample saturation). The outlet gas during both TPR and oxygen pulse chemisorption analysis was monitored and quantified by means of a thermal conductivity detector (TCD), after careful calibration. A similar apparatus, equipped with a quadrupolar mass spectrometric detector (MKS, PPT Residual Gas Analyser) was used to identify the nature of the effluent species. The total amount of oxygen adsorbed was expressed as chemisorbed oxygen volume per gram of sample (Ncm^3/g$_{cat}$) or per gram of Ru. Metal dispersion and Ru surface area were calculated as described in [31].

2.3 Activity tests

Activity tests were performed by means of a bench scale, fixed bed, down-flow Incoloy 800 reactor. A detailed description of the apparatus and procedure is given elsewhere [2]. Briefly, the catalyst in 0.15–0.25 mm particle size was loaded after dilution (1/22 vol/vol) with quartz particles of the same size, in order to minimise the hot-spot along the catalyst bed. The catalyst was activated in situ by flowing a H$_2$ + N$_2$ mixture (H$_2$/N$_2$ =

1.5/1 vol/vol), at GHSV = 20,000 h^{-1}, 30 bar, while increasing temperature following different activation programmes. Standard activation (Astd) was carried out by heating by 1°C/min up to 450°C, maintained for 5 h and then decreased down to 430°C. In order to check the effect of activation on catalytic activity, the following heating programmes were also applied: heating by 1°C/min up to 450°C, kept for 120 h (A1), or up to 550°C, kept for 5 h (A2). The reactant gas mixture was carefully purified from oxygenates by passing through a trap, packed with a proper amount of frequently regenerated, reduced Fe-based commercial ammonia synthesis catalyst.

Activity tests have been carried out under standard reaction conditions, *i.e.* 100 bar and 430°C, by varying the gas mixture space velocity from GHSV = 60,000 to 200,000 h^{-1}. The effluent gas was bubbled in a known amount of diluted H_2SO_4, followed by titration of the residual acid with NaOH solution.

3 - RESULTS AND DISCUSSION

The samples were prepared following the previously optimised procedure [2,17,25] (Table 1). In order to check the effect of different activation conditions and to identify the state of promoters, a single batch of Ru/C was used for promoters deposition. No sample treatment was done after promoters impregnation, hence precursors' decomposition was expected during catalyst activation. The latter was made by temperature programmed reduction (TPR), according to the heating programmes detailed in Table 2. The reduced samples were then analysed by oxygen pulse chemisorption. TPR with H_2 surely leads to the reduction of the RuO$_x$ surface passivated layer and to the decomposition of the nitrate promoters precursor. In addition, a higher hydrogen and oxygen uptake can be expected if

the alkaline promoters reduction occurs. On the other hand, if the structural action of Ba is true, a different oxygen uptake should be observed if the hypothesised Ru redistribution affects metal dispersion.

A further checking for support effect during activation was made by means of the comparative sample prepared with the as supplied active carbon (AC). It should be remembered that this sample does not have any practical use, due to support instability under the ammonia synthesis reaction conditions.

3.1 – TPR analysis

An example of TPR pattern is reported in Fig.1, relative to the R3 programme (Table 2). The blank Cs/GC sample showed a broad and very small H_2 uptaking peak between 350 and 450°C, corresponding to nitrate decomposition. Similar patterns were observed for the other blank samples. The Ru/GC sample showed a reduction peak centred at *ca.* 100°C, due to the reduction of RuO_x surface species. The same peak was observed when using AC as support (sample Ru/AC, not reported), but it showed much broader. The peak at higher temperature is due to incipient CH_4 formation, due to poor support stability in the absence of promoters [25].

After adding the promoters the pattern radically changed, as found also by others [29,32]. The first peak shifted towards higher temperature and became much more intense. Indeed, the maximum of the first peak was found at *ca.* 200-250°C for all the singly promoted samples supported on GC. By contrast, the nitrate precursor decomposition occurred at markedly lower temperature with respect to the blank samples. It should be noticed that the TCD detector does not permit a reliable quali- and quanti-

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fication of the various species in the case of strongly overlapping contributions. The Cs-Ru/AC sample showed the same shift of the low temperature reduction peak, whereas the higher temperature peak was practically absent. Finally, the tri-promoted sample prepared from $RuCl_3$ gave a broader reduction pattern, with higher H_2 uptake, continuing even at the highest temperature (Fig. 2).

From the TPR data the following preliminary conclusions can be drawn: i) H_2 uptake strongly increases for the promoted samples; ii) promoters precursors decomposition shifts to markedly lower temperature in the presence of Ru; iii) the reduction profile is more complex and H_2 uptake is higher for the Cs-promoted sample supported on GC, with respect to AC; iv) the chloride containing sample shows higher H_2 uptake and requires a much prolonged reduction with respect to the samples prepared from a different Ru precursor.

3.2 – O₂ chemisorption

The measurements were carried out by following the procedure reported in [31] on the samples reduced as detailed in Table 2 and then flushed with He to remove the excess H_2. The experiment was repeated at least three times on fresh portions of each sample. The number of repetitions was increased, when needed, to achieve a better reliability. A good agreement between consecutive measurements was always obtained with unpromoted samples, whereas varying O_2 uptakes were often obtained with promoted samples, especially with Cs and K, supported on GC. The results are summarised in Table 3. No significant effect of the reduction temperature on oxygen uptake of blank samples was observed. Oxygen uptake of the Ru-containing samples is reported in the same Table 3 for every reduction programme. Ru dispersion (D) and exposed surface area (S_{Ru}),

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calculated as described in [31], are reported for unpromoted samples only, due to oversized oxygen uptake by promoted catalysts (*vide infra*), leading to unreliable data.

The blank samples of the unpromoted support showed very low oxygen uptake for both supports, in line with our previous findings. The same result was obtained when adding Cs to the non-graphitised AC. By contrast, progressively higher O_2 uptake was observed with the alkali promoted samples supported on the graphitised GC.

The effect of the unpromoted Ru/GC sample (Table 3 and Fig.3) showed that the highest dispersion was obtained after treatment at the lowest temperature. By increasing temperature or prolonging the reduction up to 15 hours, the slightly decreasing of metal dispersion confirmed the expected sintering of Ru.

Some differences were observed upon Ba addition. Indeed, a much lower amount of oxygen was uptaken by the sample treated at 300°C, in line with the hypothesis of partial Ru covering by BaO [5,13,18]. Furthermore, this excludes the reduction of this promoter at least at this temperature. When the reduction temperature was increased, a bit higher oxygen uptake was observed with respect to that uptaken by the unpromoted sample at 400°C. However, a further increase of the reduction temperature or a longer reduction time did not show any difference in oxygen uptake with respect to the Ru/GC catalyst.

Cs addition brought about a considerable increase of oxygen uptake (Fig. 3), as observed also by others [29]. 300°C seems a sufficient temperature to provoke this anomalous oxygen uptake. By contrast, prolonged reduction times seem to decrease the very high amount of oxygen uptake. Similar results were obtained with sample K-Ru/GC, ranking half way between Ru/GC and Cs-Ru/GC. However, K seems less effective than Cs in increasing the oxygen uptake, in spite of its much higher concentration. Indeed, this value can be compared with that of the K-GC blank sample, which exhibits oxygen uptake

higher than Cs-GC, in contrast with the Ru-containing samples, for which oxygen over-taking is more limited for the K-promoted sample.

The extra oxygen uptake of the alkali-promoted samples can be explained in terms of reduction of the alkali metal ions during the reduction treatment, supported also by the higher intensity of the TPR pattern (Fig.1) with respect to the unpromoted sample. This hypothesis was suggested by Aika [33] and Kowalczyck [28,29], though the degree of reduction of the alkali metal is not yet completely clear. Cs^+ and K^+ reduction, at least under the present reduction conditions, seems possible if we consider chemisorbed H species (in equilibrium with molecular H_2) as the reducing agent. Hence, as observed also in [34], the presence of Ru seems fundamental in order to catalyse the surface reduction of alkali metal ions, very likely through the dissociative adsorption of H_2, so providing the atomic H needed for such a reduction. Some possible reaction pathways and the relative ΔG calculations are proposed elsewhere [33,34]. However, we have observed some overtaking of oxygen also in the case of the blank samples doped with Cs and K. This can be justified by the possible reduction of these ions even in the absence of Ru, if a proper amount of chemisorbed H species can form (*e.g.* in correspondence of some metallic impurities of the support). However, a trace of this reduction should be observed during TPR, which is not our case (Fig.1). Another possible explanation can be the oxidative interaction between the support and the alkali metal ion, leading to some oxidised surface compound (such as carbonate or carbonyl species). At the moment we don't have any evidence for this. Finally, the stability of different Cs oxide species, characterised by higher O/Cs ratio, can partly explain the higher uptake of oxygen for the Cs doped samples. However, when Ru is present, a much higher oxygen uptake was observed with Cs, which cannot be explained on this basis only. Finally, no evidence of BaO reduction can be drawn from these data. However, the hypothesis of a structural action of this promoter cannot be excluded.

Another important point is the role of the support in this reduction process. It is well known that alkaline metals can interact with graphite to form intercalation compounds [35,36]. Hence, it can be hypothesised that the alkaline promoters are reduced during the activation process, the reaction being favoured by the formation of intercalation compounds. It is also well known that the AC stability under the ammonia synthesis conditions is poor [2,25,37-39] and that it can be improved by a proper thermal treatment and by the addition of promoters [25]. During heating in inert atmosphere, the carbon support is partially graphitised, the graphitisation degree depending on temperature and time of treatment [2]. Hence, the graphitised carbon support can help the formation of intercalation compounds with the reduced alkaline metals. This hypothesis was checked by preparing a comparative sample supported on the non-graphitised AC. The oxygen uptake of this sample, reduced at different temperatures before and after Cs addition, is reported in Table 3 and Fig.4. The unpromoted catalyst supported on AC showed a slightly higher dispersion with respect to the GC-supported one, in line with our previously reported data [31]. However, when adding Cs to Ru/AC, the same O_2 uptake was observed, independently of the reduction temperature. This further confirms the hypothesis of Cs reduction over partially graphitised support only. Indeed, in the absence of the stabilisation effect due to the formation of the intercalated reduced promoter, neither H_2 (during TPR, Fig.1) nor O_2 (during chemisorption, Fig.4) over-taking was observed.

The same samples were analysed by N_2 adsorption/desorption, both as prepared and after reduction at 480°C (Table 4). The Cs-promoted, AC-supported samples showed a little decrease of SSA after reduction at 480°C, whereas the opposite trend was observed for the GC-supported one. One may conclude that inter-lamellar collocation of at least a part of the promoter can increase not only pore volume, but also surface area.

Furthermore, the support can play an important role also as electron transfer agent. Indeed, a *hot-ring promotion* has been suggested for Cs [13,40]. The latter would locate at

the interface between Ru and the support, so to ensure electron donation between the reduced promoter and the active metal. If Cs is reduced and forms an intercalation compound, this scheme can be overcome. Indeed, the graphitic layer itself can act as a transfer medium for electron donation to Ru, so maximising the promoter efficiency and possibly allowing to decrease its concentration.

Therefore, from the present data one may conclude that Cs, and, to a lower extent, K, play an electronic promotional effect in the reaction, especially when the support is graphitised. Indeed, in the latter case the reduction of at least a part of the promoter is favoured by the stabilising formation of intercalation compounds, which maximises the promoters' activity. It should be underlined that Cs (or K) as promoters are active in ammonia synthesis also when used with AC, though their reduction in this case is unlikely (*vide supra*). Indeed, it has been shown by XPS analysis [1,25] that, even if present in their oxidised form, these promoters, as well as BaO, show some electron-donor effect, leading to a shift of Ru binding energy. However, without proper support environment, the effect of K and Cs is very weak with respect to BaO. As for the latter, the mentioned XPS measurements [25], later confirmed by others [18,27], show that undoubtedly BaO has an electronic effect. However it is hard to correlate this moderate action with its overperforming activity. Indeed, the BaO-induced shift of Ru binding energy is rather low if compared with the Cs-induced one. Moreover, the calculated electronegativity of BaO is similar to that of CsOH [27]. By contrast, its effect in promoting catalyst performance is much higher than expected from these findings. Therefore, a structural effect, as hypothesised in [28] or in [41], should not be excluded.

In our previous investigation on promoters effect [25] we reported on the role of Ba, Cs and K on the stability of the support towards methanation. It was found that, in addition to partial graphitisation through thermal treatment, carbon stability can be strongly improved by proper promoters addition. Indeed, CH_4 formation was shifted towards higher

temperature and decreased considerably after Ba addition. Further improvement was attained by adding also K and Cs.

The support stabilising effect of Ba can be explained on the basis of a proposed model of Ba deposition on Ru [13,18]. TEM images showed that BaO partly covers the Ru particles. In particular, for these catalysts it has been demonstrated that optimal Ru dispersion should not be too high (due to the structure sensitivity of the ammonia synthesis), so to have an average particle size of *ca.* 2 nm. This would maximise the formation of the so-called B5 active sites located on steps in monolayer surface terraces. These sites seem the most active for N_2 adsorption, whereas H_2 can dissociate non-selectively also on other Ru sites (and compete with N_2). In this scenario we can hypothesise that BaO can accommodate on Ru terrace sites, which can dissociatively adsorb H_2, so limiting the concentration of surface active hydrogen which can react with the support. This would not affect catalytic activity (because H_2 dissociation is not the rate determining step of the reaction), but it would strongly limit the unwanted methanation of the support, otherwise catalysed by unpromoted Ru even on graphitised carbon. The stabilising effect of K and Cs is less clear. We can hypothesise that the above mentioned formation of intercalation compounds can modify both support structure (by increasing the interlayer distance) and electronic state (by varying the Fermi level energy), so further improving support resistance.

3.3 – Catalyst activation

On the basis of the above reported results the role of the activation step becomes more critical. Indeed, if the promoters have to be reduced and/or if catalyst reorganisation takes place, the activation step should be optimised, so to attain the best performing conditions. This was particularly stressed by Hinrichsen *et al.* [30], who showed the need

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of prolonged high temperature reduction to allow high and stable catalytic activity for Ba-Ru/MgO catalysts. Fig. 1 and 3 show that, from the point of view of Ru dispersion and possible promoters reduction, there is no need of a too high pre-treatment temperature and that a reduction time as long as 15 h seems detrimental from both points of view for Ru/C. To check the effect of activation on catalytic activity some ammonia synthesis tests have been here made after activation, under different conditions, of fresh portions of one of our best-performing catalysts. The results are reported in Fig. 5. It is evident that the increase of both the temperature and the duration of reduction brings about a decrease of catalytic activity, in line with the results reported in Fig.3, showing the decrease of oxygen uptake for the Cs-promoted sample.

A possible reason of this discrepancy between our data and those reported elsewhere [30] could be the higher tendency to sintering when the support is carbon rather than MgO. However, we believe that the keypoint is the nature of Ru precursor (nitrosylnitrate in the present case, chloride in most of the other samples) requiring different and more or less drastic activation conditions. The need of catalyst washing until complete chloride elimination, for a sample prepared from $RuCl_3$, has been already shown by us [17]. The TPR pattern (Fig.2) helps in clarifying this point. Indeed, the TCD peak does not close within the experimental time lapse, at difference with what reported for a comparative sample prepared from $Ru(NO)(NO_3)_3$. Hence, we can hypothesise that the samples prepared from $RuCl_3$ have to be activated more drastically, so to remove chlorides, well known poisons for this catalyst [1,17,32,34]. This "over-activation" could be avoided by a repeated washing of the sample after Ru reduction, leading to good catalyst performance even with a shorter activation [17]. This was confirmed by monitoring the out-coming gas during catalyst activation, showing the presence of chlorides, which were not completely removed during catalyst reduction.

4 - CONCLUSIONS

The influence of the reduction treatment under various temperature and duration conditions was analysed for a set of Ru/C catalysts for ammonia synthesis. High H_2 uptake during reduction and anomalous O_2 uptake during chemisorption were observed for alkali-doped samples with graphitised carbon as support. This can be explained by the possible partial reduction of Cs, and, to a lower extent, of K, favoured by the formation of intercalation compounds within the lamellar graphite layers. No evidence of BaO reduction was observed. However, its electronic-only role seemed insufficient to justify its high promoting activity. Some hypotheses have been suggested to explain the effect of the promoters in improving the support stability against methanation. In particular Ba can cover some Ru terrace sites, so reducing the activation of H_2 for this unwanted reaction. Finally, the nature of Ru precursor plays a considerable role in defining the activation procedure of the final catalyst.

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Table 1: Composition of the samples prepared.

Catalyst	support[b]	K/C wt%	Cs/C wt%	Ba/C wt%	Blank samples	support[b]	K/C wt%	Cs/C wt%	Ba/C wt%
Ru/GC[a]	GC	-	-	-	-	-	-	-	-
Cs-Ru/GC	GC	-	5.69	-	Cs/GC	GC	-	6.32	-
Ba-Ru/GC	GC	-	-	3.63	Ba/GC	GC	-	-	3.84
K-Ru/GC	GC	4.81	-	-	K/GC	GC	4.61	-	-
Ru/AC	AC	-	-	-	-	-	-	-	-
Cs-Ru/AC	AC	-	4.64	-	Cs/AC	AC	-	4.74	-

[a] Ru loading: Ru/C = 3.8 wt%
[b] GC: graphitised carbon, SSA = 280 m^2/g; AC: active carbon, SSA= 1400 m^2/g

Table 2: TPR programs used to study the effect of temperature and time of reduction.

Programme	Reduction[a]		Flushing[b]	
	T	time *(h)*	T	time *(h)*
R1	300	1	350	1
R2	400	1	450	1
R3	480	1	480	2
R4	400	5	450	1
R5	400	15	450	1

[a] TPR: 5% H_2/Ar mixture, total flow rate: 40 cm^3/min, heating rate: 10°C/min
[b] flushing with He, flow rate: 40 cm^3/min, heating rate: 10°C/min

Table 3: O_2 uptake of various samples. Reduction programmes as detailed in Table 2.

S_{Ru}=Surface area of exposed Ru, D=Ru dispersion, both calculated as reported in [31].

Sample	Programme	V_{blank} Ncm^3/g_{cat}	V_{cat} Ncm^3/g_{cat}	V_{Ru} Ncm^3/g_{Ru}	S_{Ru} m^2/g_{Ru}	D
Ru/GC	R1	0.2	2.41	62.17	205.15	55.95%
	R2	0.2	1.68	41.83	138.04	37.65%
	R3	0.2	1.67	41.44	136.76	37.30%
	R4	0.2	1.71	44.16	145.72	39.74%
	R5	0.2	1.41	34.49	113.82	31.04%
Cs-Ru/GC	R1	1.20	3.87	77.68	/	/
	R2	1.20	3.80	77.11	/	/
	R3	1.20	3.94	79.74	/	/
	R4	1.20	2.97	52.05	/	/
	R5	1.20	3.04	54.01	/	/
Ba-Ru/GC	R1	0.40	0.91	14.70	/	/
	R2	0.40	2.52	61.76	/	/
	R3	0.40	1.78	39.41	/	/
	R4	0.40	1.62	34.68	/	/
	R5	0.40	1.71	37.25	/	/
K-Ru/GC	R1	1.88	2.95	33.89	/	/
	R2	1.88	2.65	24.87	/	/
	R3	1.88	2.59	23.31	/	/
Ru/AC	R1	0.20	2.53	65.39	215.79	58.85%
	R2	0.20	2.02	51.18	168.89	46.06%
	R3	0.20	2.51	64.82	213.91	58.34%
Cs-Ru/AC	R1	0.20	2.47	67.74	223.53	60.96%
	R2	0.20	2.07	52.42	172.97	47.17%
	R3	0.20	2.54	69.95	230.83	59.55%

Table 4: Specific surface area (SSA), Pore volume (V_p) and average pore diameter (D_{Av}) of selected samples before and after reduction (ramp R3).

Sample	Fresh sample			After reduction at 480°C		
	SSA (m^2/g)	V_p (cm^3/g)	D_{av} (nm)	SSA (m^2/g)	V_p (cm^3/g)	D_{av} (nm)
Cs/GC	205	0.34	67	253	0.44	70
Cs/AC	1164	0.69	23	1130	0.65	23
Ru/GC	180	0.22	48	169	0.22	52
Cs-Ru/GC	119	0.15	49	150	0.22	59
Ru/AC	968	0.59	24	962	0.54	24
Cs-Ru/AC	972	0.47	24	953	0.37	24

FIGURE CAPTIONS

Fig. 1: Example of TPR pattern (programme R3, Table 2).

Fig. 2: TPR analysis of a Cs+Ba+K-Ru/GC sample prepared from $RuCl_3 \cdot 3H_2O$. Reduction programme R2, Table 2.

Fig. 3: Oxygen uptake vs. reduction treatment for variously promoted GC samples.

Fig. 4: Effect of the support on oxygen uptake of the unpromoted and Cs-doped samples.

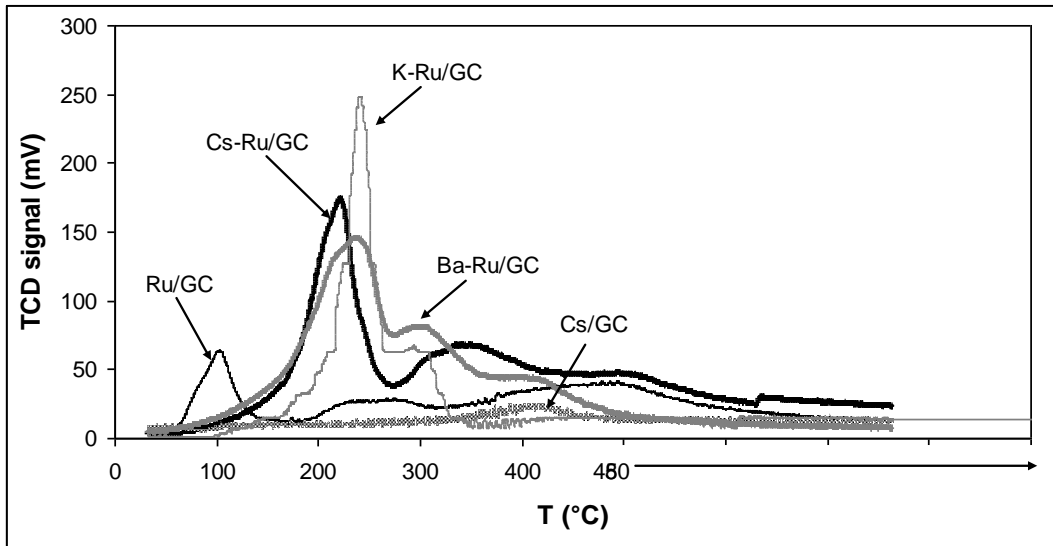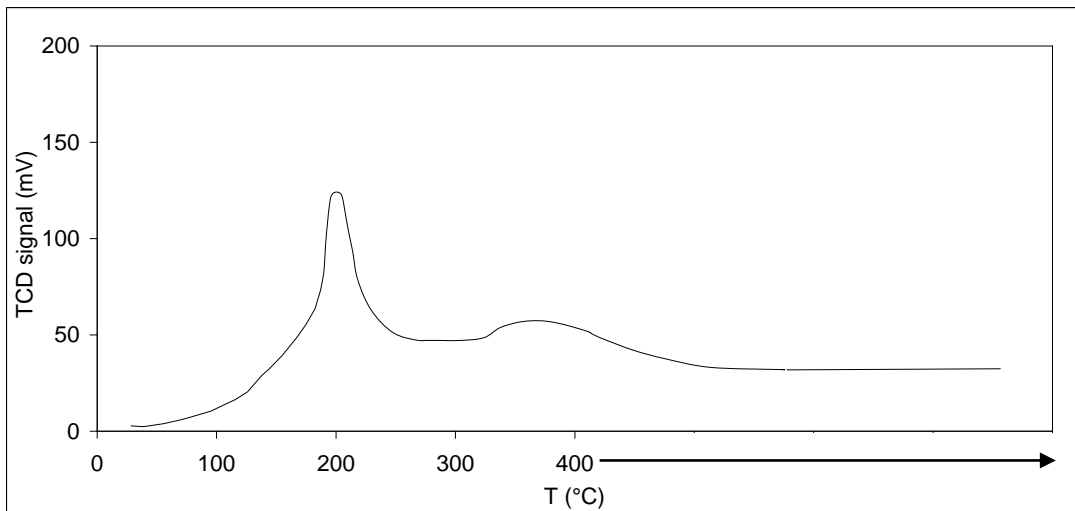**Fig. 5:** Dependence of catalytic activity on activation temperature and time. Heating rate: 1°C/min.
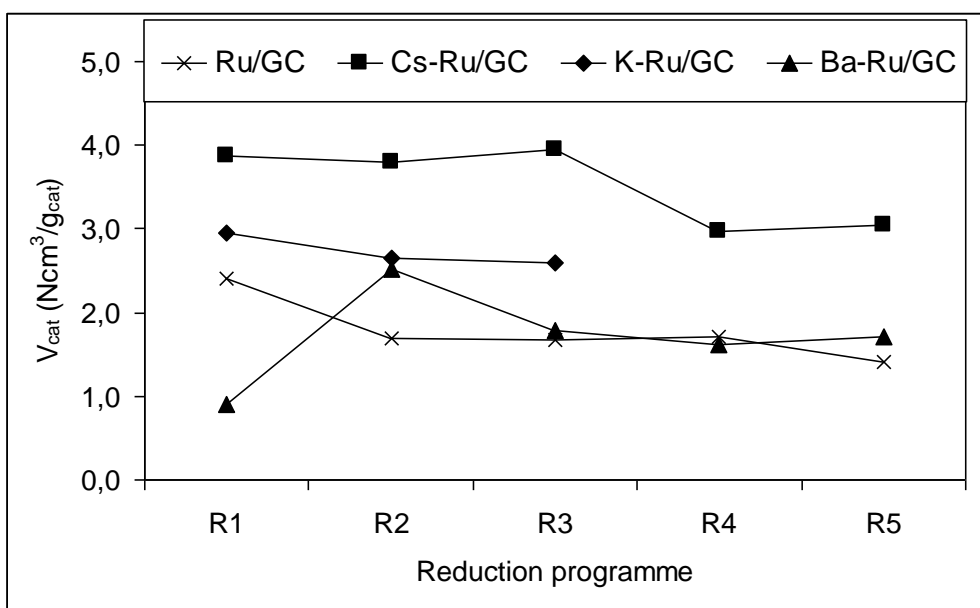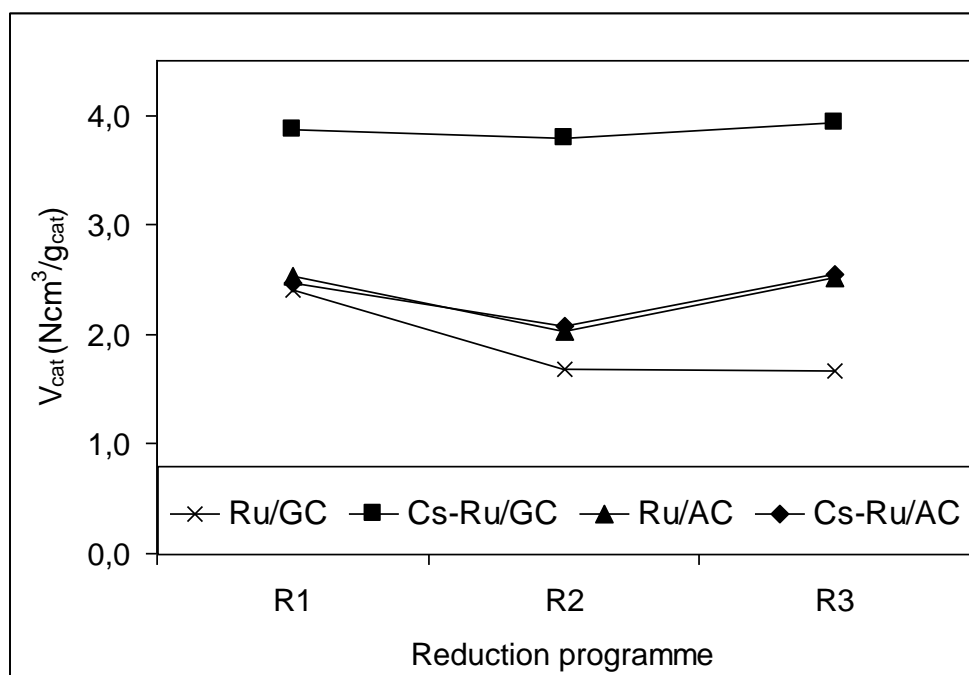
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig.5