Ru/MgO sol-gel prepared catalysts for ammonia synthesis

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A new method of preparation of alkali-promoted Ru/MgO catalysts, based on a sol-gel procedure, starting from magnesium ethoxide, $Ru_3(CO)_{12}$ and a cesium compound has been designed. The gels were subjected to an activation/reduction procedure to substantially obtain Ru-CsOH/MgO. The activated catalysts were tested in ammonia synthesis at atmospheric pressure. It was clear that the sol-gel prepared Cs-promoted Ru/MgO catalysts are much more active, under the same reaction conditions, than the analogous catalysts prepared by impregnation procedures.

KEY WORDS: ruthenium-based catalyst; preparation; characterization; sol-gel; ammonia synthesis.

1. Introduction

Alkali-promoted Ru catalysts are a very promising alternative to the traditionally used Fe catalysts for ammonia synthesis also at high pressure. It was recently demonstrated that the activity of a Cs_2CO_3-Ru/MgO catalyst, prepared by an impregnation method from $Ru_3(CO)_{12}$, at 50 bar is quite similar to an industrially used multiply-promoted Fe catalyst at 100 bar, at about the same space velocity and temperature [1].

However, supported Ru catalysts, prepared by sol-gel methods from $Ru_3(CO)_{12}$, are much more active than the impregnated ones in other reactions, such as CO hydrogenation [2,3].

Recently, MgO was prepared by a sol-gel method, which consists of hydrolysis of a magnesium alkoxide in the presence of acidic or basic catalysts, followed by a polycondensation reaction [4].

In this work, a new method of preparation of Ru/MgO and Cs-promoted Ru/MgO catalysts, based on a sol-gel procedure, has been designed.

2. Experimental

2.1. Catalyst preparation

Initially, a Cs-Ru/MgO impregnated catalyst was prepared according to the literature method [1]. The MgO support (Engelhard) was heated in air at 773 K for 6 h and then dispersed in a stirred solution of $Ru_3(CO)_{12}$ in dry THF for 4 h, in nitrogen atmosphere, at room temperature. After evaporating the solvent at 313 K, the slightly orange powder was slowly heated in a microreactor under helium flow up to 723 K to decompose the carbonyl precursor to give Ru/MgO, dark grey. Cs_2CO_3-Ru/MgO was then prepared by impregnation with a solution of Cs_2CO_3 in absolute ethanol. After stirring the suspension for 3 h, the solvent was evaporated and the solid was dried in vacuum. Finally, the catalyst was reduced by heating in a microreactor up to 673 K in a flow of synthesis gas, $N_2 + 3H_2$.

Ru/MgO was sol-gel prepared as follows. Magnesium ethoxide was dissolved in refluxing H_2O-ethanol, then the solution was cooled to room temperature and a solution of $Ru_3(CO)_{12}$ in dry THF was added, constantly stirring until the gel was obtained. After drying in vacuum, the grey solid was charged in a microreactor and slowly heated (2 K/min) under a flow of synthesis gas up to 723 K.

The Cs-promoted Ru/MgO catalysts were sol-gel prepared by the same procedure as above, but adding after $Ru_3(CO)_{12}$-THF the solution of a Cs compound: CsN_3, Cs_2CO_3 or $Cs_2(COO)_2$. The activation has been performed by slowly heating (2 K/min) in helium up to 573 K, then the catalysts were reduced in a flow of hydrogen for 2 h. Some sol-gel prepared catalysts were activated and reduced at different temperatures: 573, 623 and 673 K.

In all prepared catalysts the amount of Ru was 5% by weight (as metal) on MgO, while the Cs/Ru atomic ratio always was 1 : 1.

2.2. Catalyst characterization

The catalysts were characterized by FTIR, XRD and TEM analyses, then tested in the ammonia synthesis

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from $N_2 + 3H_2$ at atmospheric pressure in a flow microreactor, by measuring the ammonia concentration in the effluent gases at different reaction temperatures by a GC-analysis on-line or the mean ammonia productivity at constant temperature, by absorbing the effluent gases in a titrated HCl solution.

3. Results and discussion

The FTIR spectra of the solid samples obtained after impregnation of MgO with the $Ru_3(CO)_{12}$-THF solution (figures 1 and 2) and after co-gelation of $Mg(OEt)_2$ in H_2O-EtOH with $Ru_3(CO)_{12}$-THF (figures 3 and 4) show some very evident differences. A narrow and intense band at 3699 cm^{-1}, associated with an OH frequency that does not form a hydrogen bond, only appears in the sol-gel prepared sample, due to the formation of hydroxide groups by hydrolysis of the alkoxide ones. The reactions that occur are [4]:

Hydrolysis

$$Mg(OEt)_2 + H_2O \rightarrow Mg(OH)(OEt) + EtOH$$

$$Mg(OH)(OEt) + H_2O \rightarrow Mg(OH)_2 + EtOH$$

Condensation

$$\text{-Mg–OEt} + \text{-Mg–OH} \rightarrow \text{-Mg–O–Mg-} + \text{EtOH}$$

$$\text{-Mg–OH} + \text{-Mg–OH} \rightarrow \text{-Mg–O–Mg-} + H_2O$$

$$\text{-Mg–OEt} + \text{-Mg–OEt} \rightarrow \text{-Mg–O–Mg-} + \text{EtOEt}$$

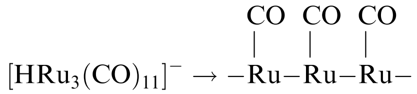
Moreover, the pattern of the bands in the carbonyl region clearly shows that in the case of the impregnation procedure $Ru_3(CO)_{12}$ is only physisorbed on the MgO surface, while in the sol-gel preparation a chemisorption occurs, certainly due to the reaction between $Ru_3(CO)_{12}$ and the hydroxide groups on the surface of the support. In fact, the spectrum of figure 2 is identical to that of solid $Ru_3(CO)_{12}$, while the corresponding spectrum in figure 4 shows two more intense bands at 2044 and 1968 cm^{-1}, respectively. These are shifted at lower frequencies than the twin bands commonly attributed to dicarbonylated Ru^{II} species, *i.e.* those formed by reaction of $Ru_3(CO)_{12}$ with the OH groups present on the surface of acid alumina [5]. Probably, a hydridocarbonyl anionic cluster initially forms as the result of the nucleophilic attack of the basic surface OH groups of magnesia at coordinated CO [6]:

$$Ru_3(CO)_{12} + \text{H–O–Mg<} \rightarrow CO_2 + [HRu_3(CO)_{11}]^-(Mg^{2+})_{1/2}$$

Then the simultaneous formation probably occurs of oxidized Ru^{II} carbonyl complexes and metal Ru particles covered with CO, according to the reactions

$$[HRu_3(CO)_{11}]^- \rightarrow Ru^{II}(CO)_n(OMg<)_2 \quad (n = 2, 3)$$

and



$$[HRu_3(CO)_{11}]^- \rightarrow \begin{array}{c}\text{CO}\quad\text{CO}\quad\text{CO}\\ |\qquad\;|\qquad\;|\\ \text{–Ru–Ru–Ru–}\end{array}$$

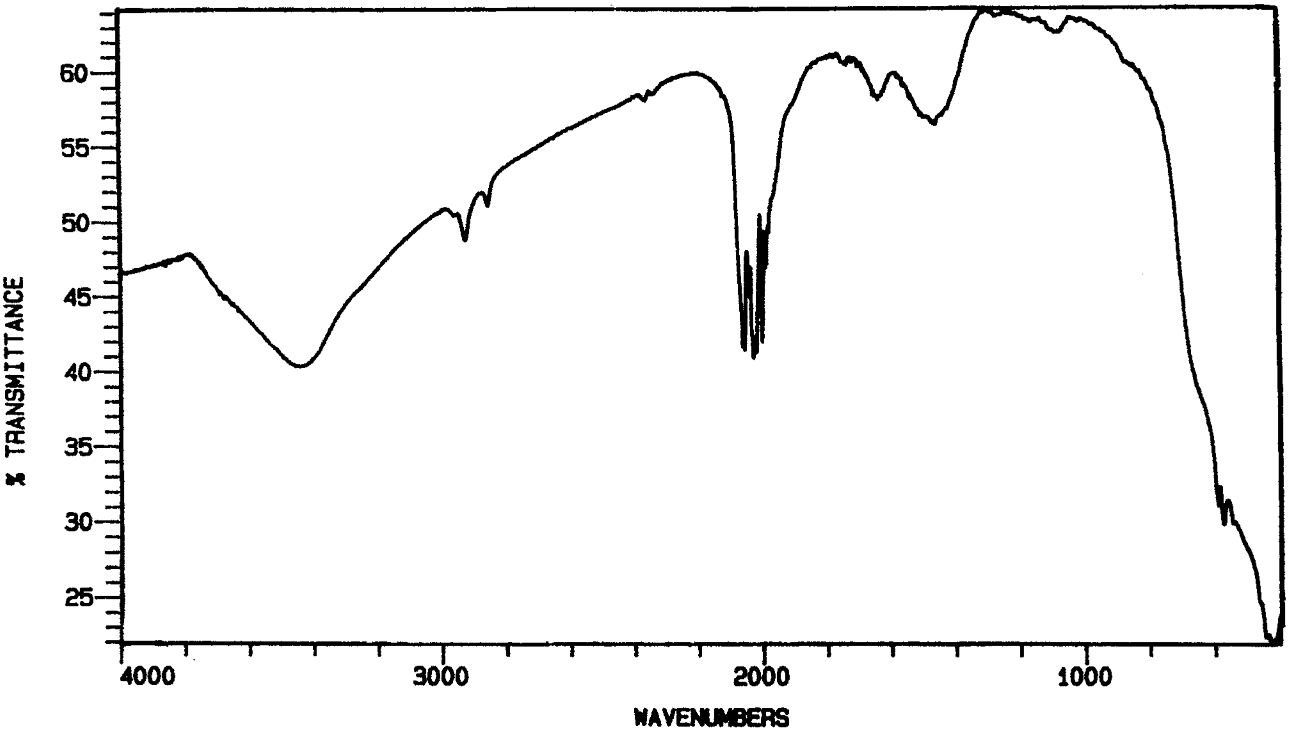


Figure 1. FTIR spectrum of the solid obtained after impregnation of MgO (Engelhard) with $Ru_3(CO)_{12}$ in THF solution (complete range 4000–400 cm^{-1}).

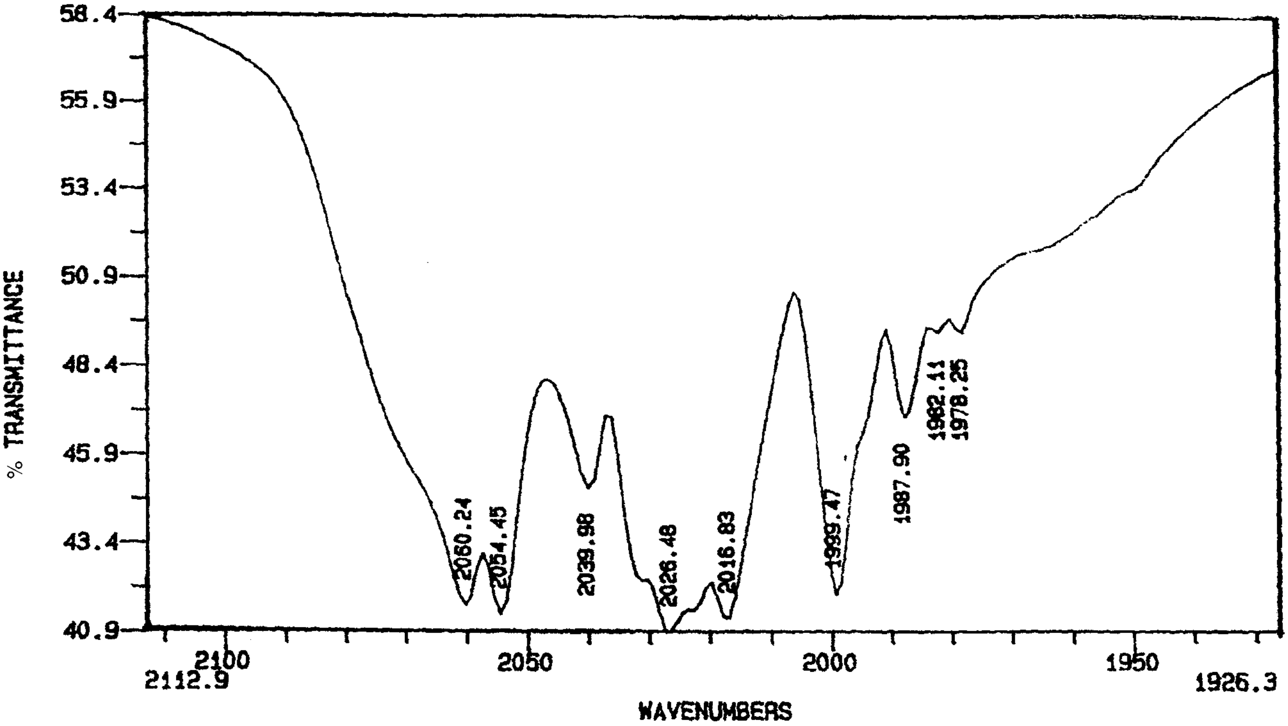


Figure 2. FTIR spectrum of the solid obtained after impregnation of MgO (Engelhard) with $Ru_3(CO)_{12}$ in THF solution (carbonyl region).

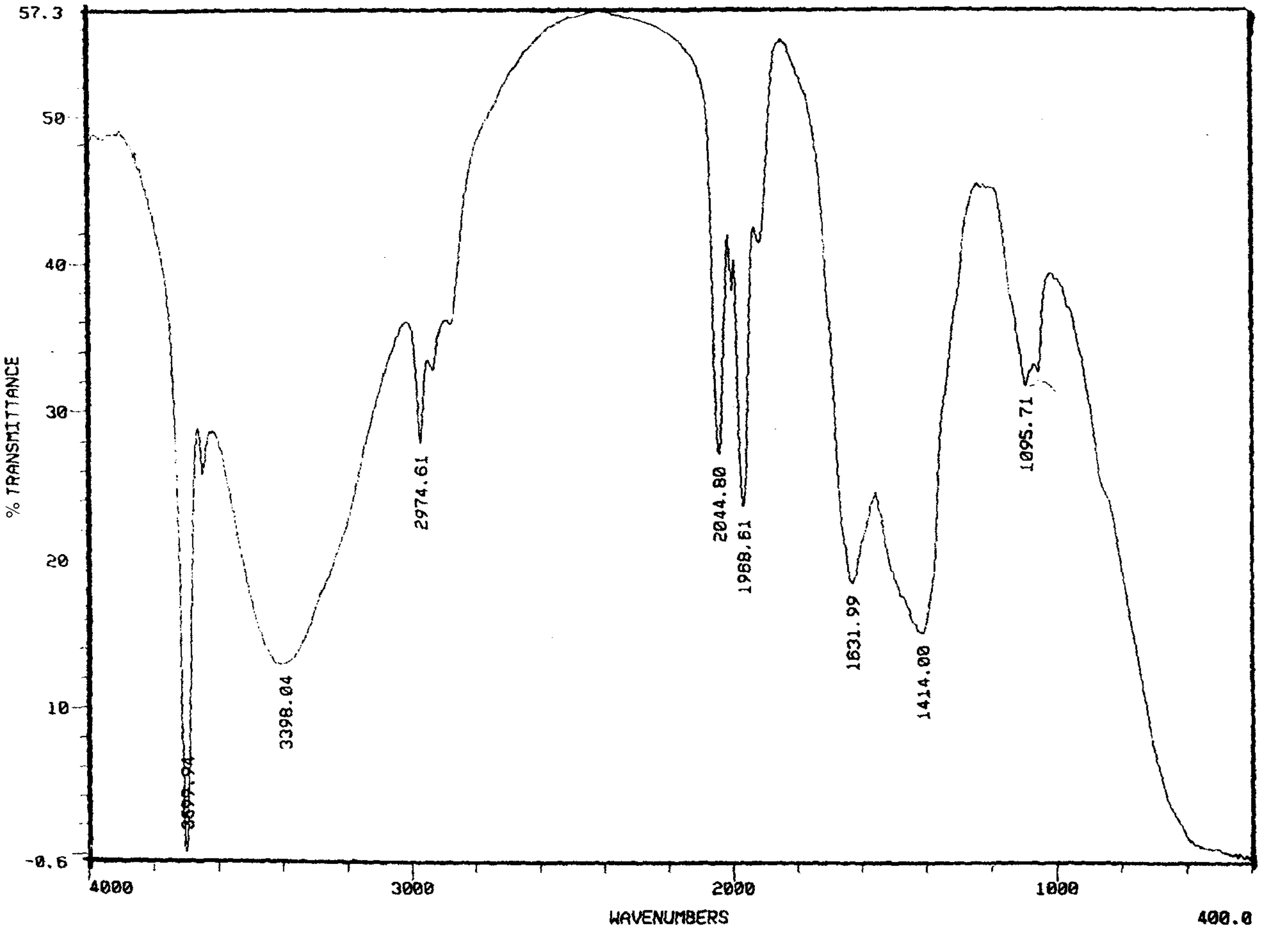


Figure 3. FTIR spectrum of the gel obtained after mixing $Mg(OEt)_2$ in H_2O-EtOH with $Ru_3(CO)_{12}$ in THF solution (complete range 4000–400 cm^{-1}).

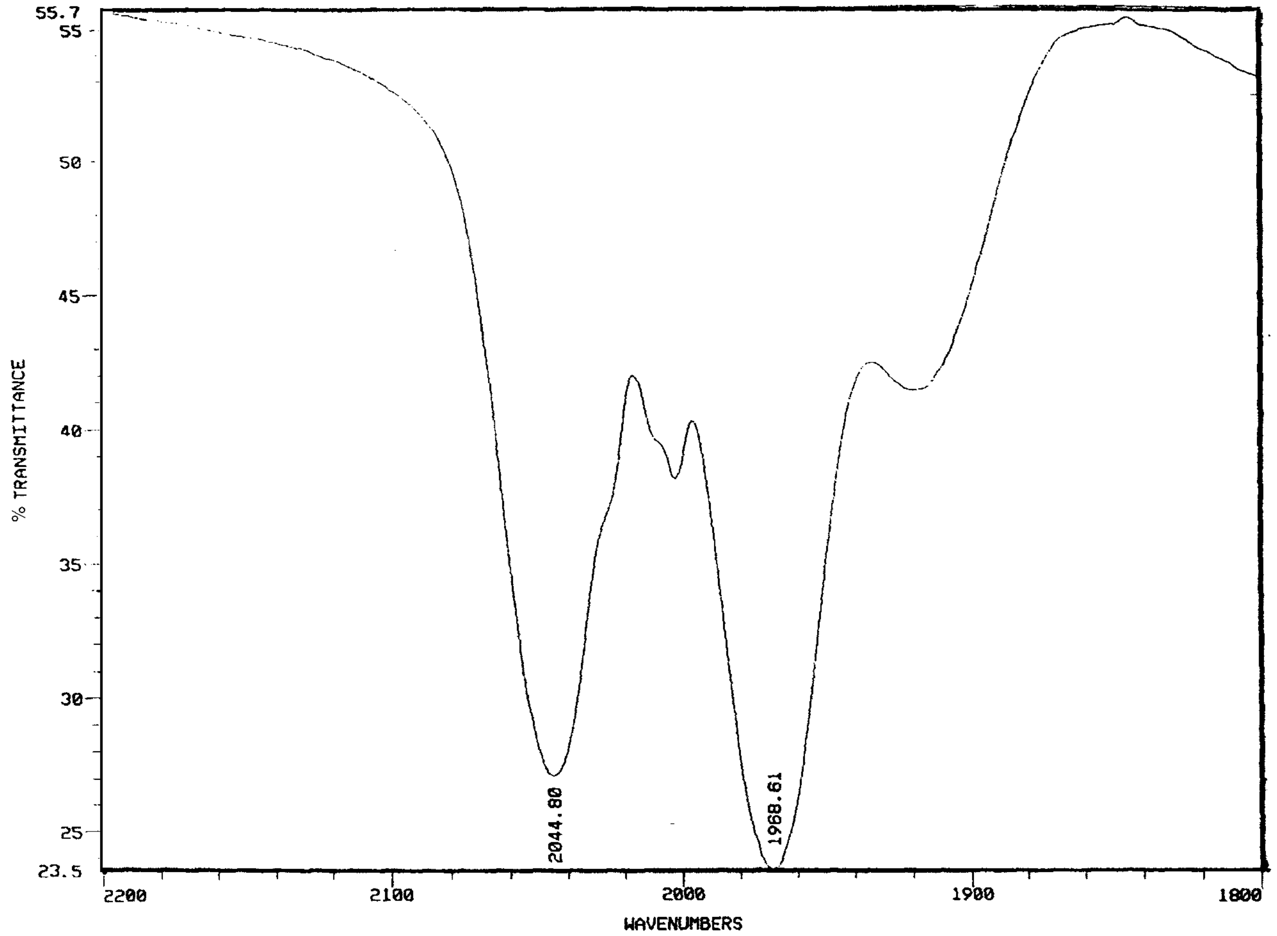


Figure 4. FTIR spectrum of the solid obtained after mixing $Mg(OEt)_2$ in H_2O-EtOH with $Ru_3(CO)_{12}$ in THF solution (carbonyl region).

The FTIR spectra of the gel obtained after mixing $Mg(OEt)_2$ in H_2O-EtOH with $Ru_3(CO)_{12}$ in THF solution and $Cs_2(COO)_2$ in H_2O-EtOH (figures 5 and 6) clearly show that the presence of the cesium compound does not influence at all the chemisorption reactions between $Ru_3(CO)_{12}$ and the hydrolysis/condensation products of $Mg(OEt)_2$.

The activated/reduced Cs-Ru/MgO catalysts prepared by impregnation and sol-gel procedures were tested for their catalytic activity in the ammonia synthesis at atmospheric pressure from a gaseous mixture $N_2 + 3H_2$ in a flow microreactor (about 2 g of charge). Figures 7 and 8 show a comparison between the results obtained with the best impregnated catalyst (CATBEST1: Cs added as carbonate) and the best sol-gel prepared catalyst (CATBEST2: Cs added as oxalate) concerning the ammonia concentration in the effluent gases and the ammonia hourly productivity, respectively, in the 440–620 K temperature range. In figure 7 the ammonia concentration equilibrium curve is also reported, as calculated from literature data [7]. The sol-gel prepared catalyst afforded its maximum activity at about 500 K, while an equivalent amount of the impregnated one achieved its maximum activity value (about 6 times lower) only at 590 K.

Even more significant indications were obtained from the ammonia synthesis tests performed at constant temperature (573 K, 0.5 g of catalyst), as reported in table 1. The ammonia productivity of the best sol-gel prepared catalysts was about 15 times higher than that of the impregnated one. Moreover, the data of table 1 evidence the role of cesium as promoter (the unpromoted sol-gel prepared catalyst is totally inactive) and the influence of the choice of cesium compound during the sol-gel preparation. In this regard it needs to reach the best compromise between converting as much as possible of the cesium compound used to CsOH (or Cs_2O) and limiting the aggregation of the Ru metal particles, which increases at increasing temperatures. The choice of $Cs_2(COO)_2$, more easily decomposable than Cs_2CO_3 or CsN_3, was then the optimum one, together with an activation/reduction temperature not higher than 623 K.

The XRD spectra shown in figure 9 provided good confirmation of the above statement. In fact, the spectrum of the sample activated up to 623 K (a) only

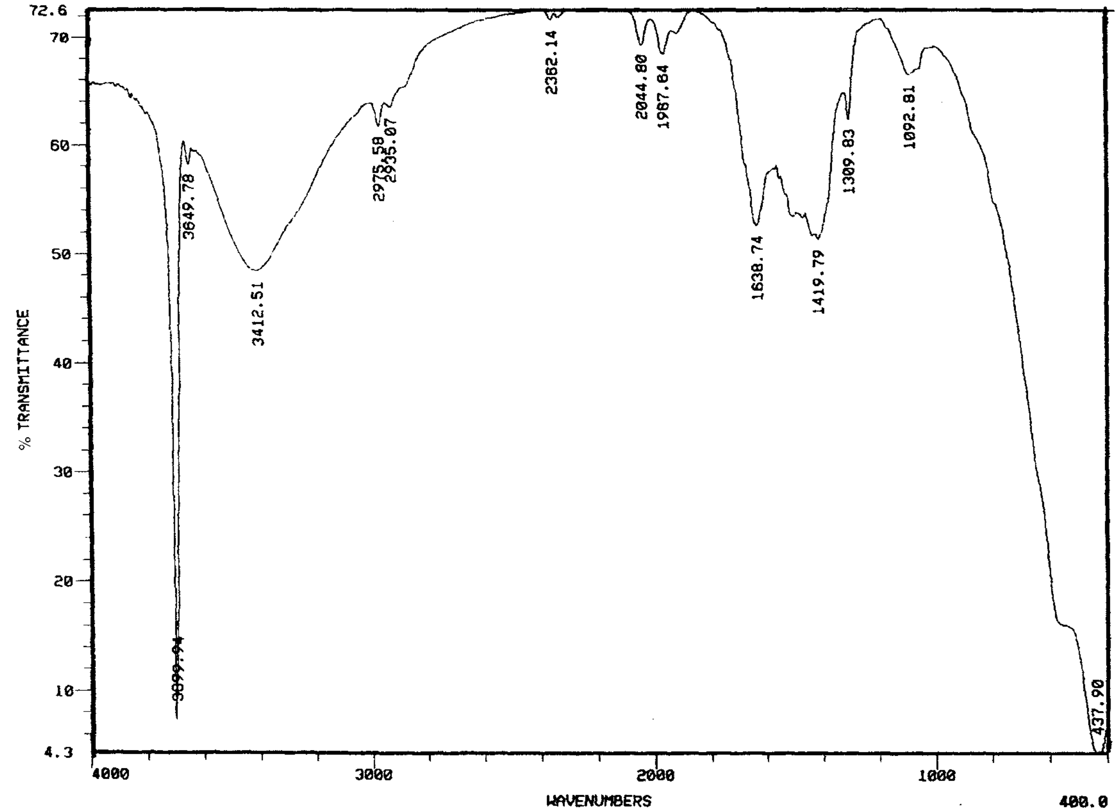


Figure 5. FTIR spectrum of the solid obtained after mixing $Mg(OEt)_2$ in H_2O-EtOH with $Ru_3(CO)_{12}$ in THF and $Cs_2(COO)_2$ in H_2O-EtOH (range 4000–400 cm^{-1}).

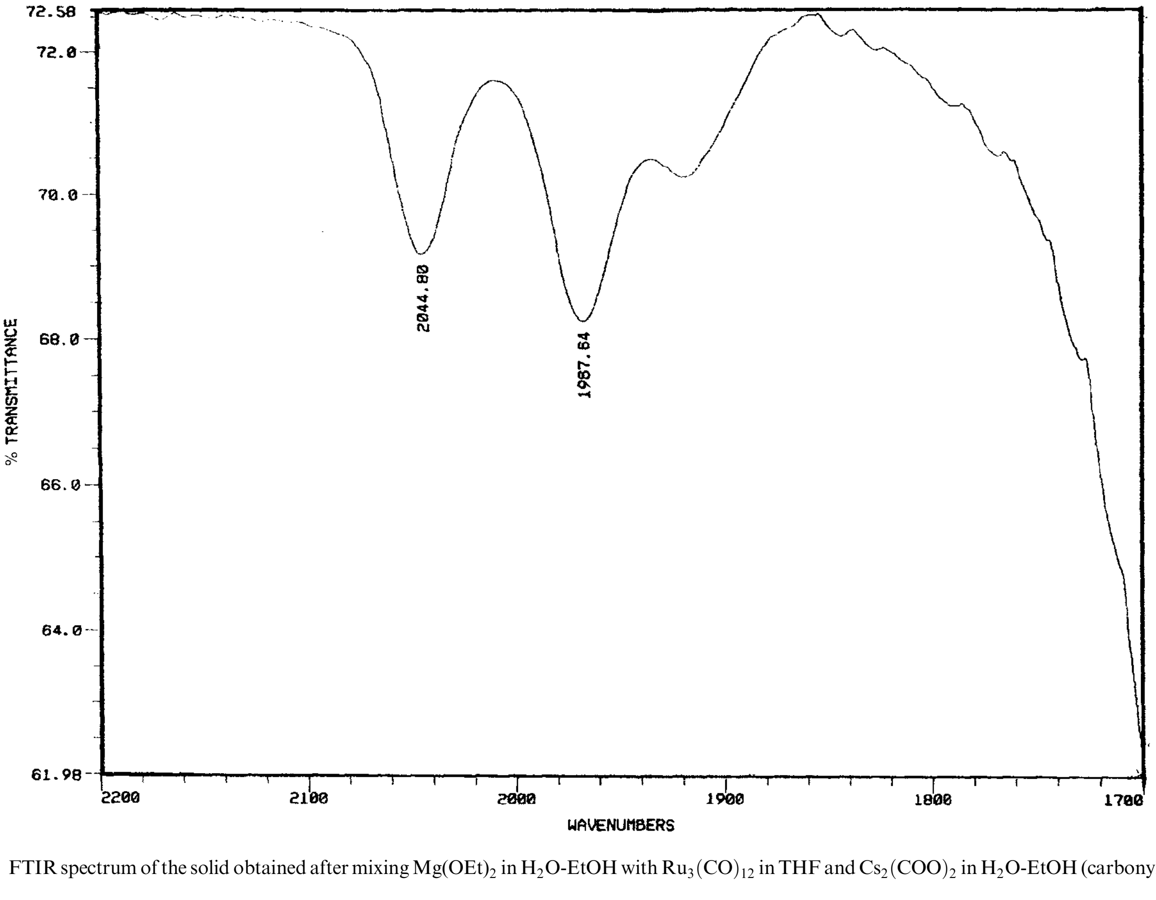


Figure 6. FTIR spectrum of the solid obtained after mixing $Mg(OEt)_2$ in H_2O-EtOH with $Ru_3(CO)_{12}$ in THF and $Cs_2(COO)_2$ in H_2O-EtOH (carbonyl region).

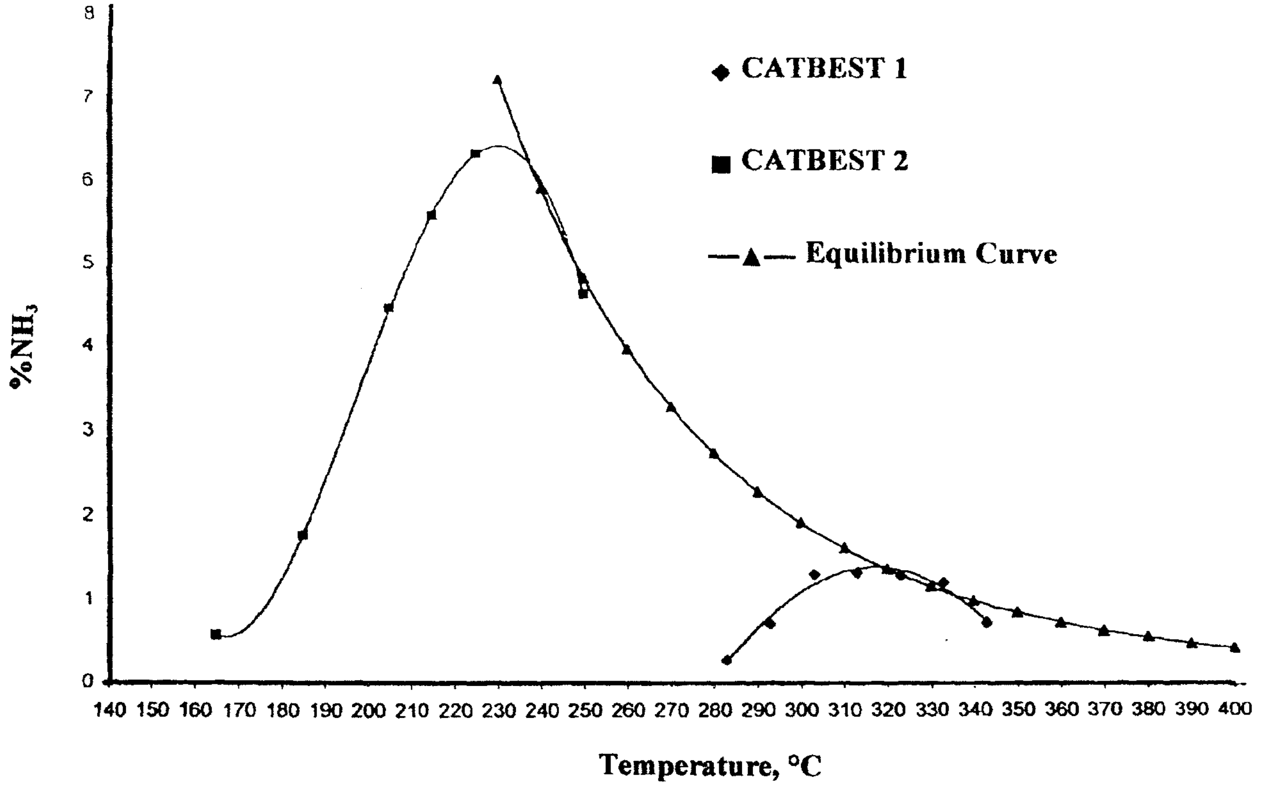


Figure 7. Ammonia concentration in the effluent gases from $N_2 + 3H_2$ reaction at atmospheric pressure, as a function of temperature (CATBEST1: impregnated Ru-Cs/MgO catalyst; CATBEST2: sol-gel Ru-Cs/MgO catalysts).

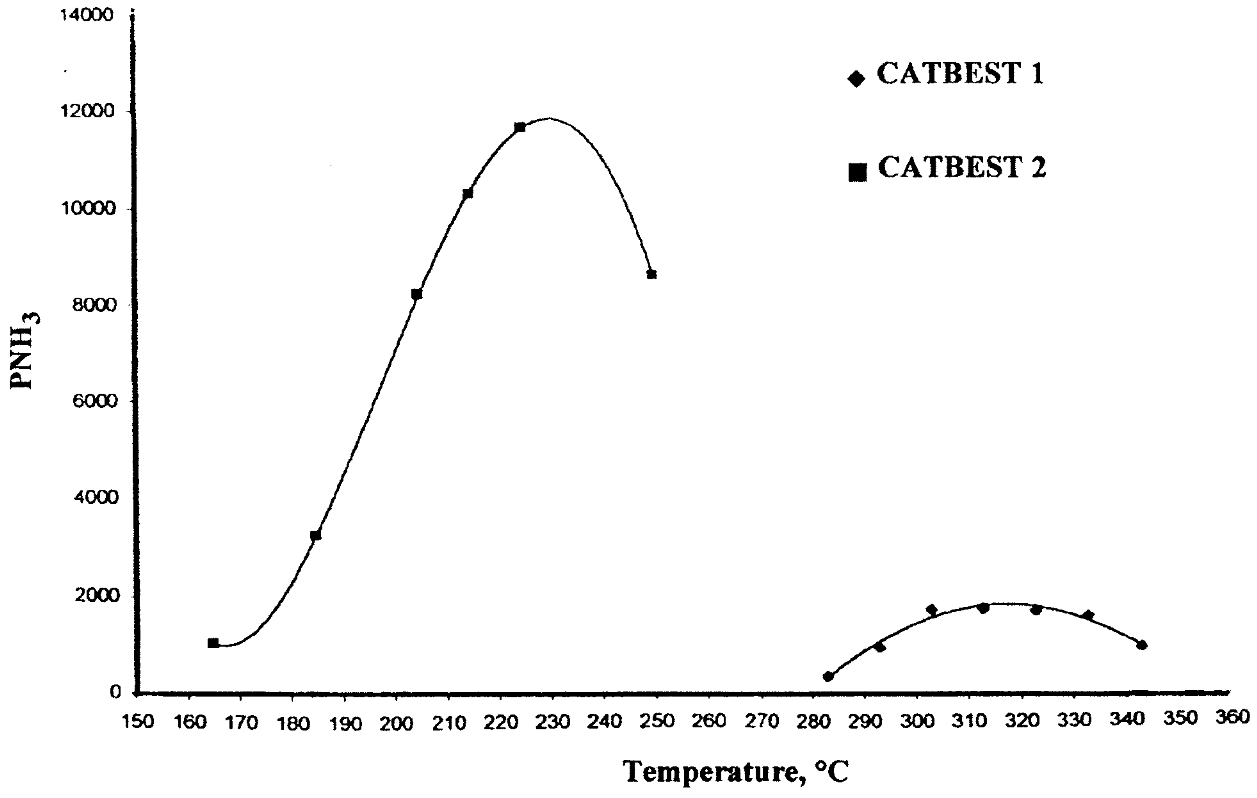


Figure 8. Ammonia productivity (ml $NH_3\ g_{cat}^{-1}\ h^{-1}$) in the ammonia synthesis at atmospheric pressure, as a function of temperature (CATBEST1: impregnated Ru-Cs/MgO catalyst; CATBEST2: sol-gel Ru-Cs/MgO catalysts).

Table 1
Ammonia mean hourly productivity (AMHP, mmol $NH_3\ g_{cat}^{-1}\ h^{-1}$) in the ammonia synthesis from $N_2 + 3H_2$ at constant temperature (573 K)

Catalyst	AMHP	Catalyst	AMHP
Ru/MgO (impr.) + Cs_2CO_3 (act. 673 K)	0.10	Ru + Cs_2CO_3/MgO (sol-gel) (act. 673 K)	1.33
Ru + Cs_2CO_3/MgO (sol-gel) (act. 623 K)	0.72	Ru + CsN_3/MgO (sol-gel) (act. 673 K)	1.25
Ru + CsN_3/MgO (sol-gel) (act. 623 K)	1.06	Ru + $Cs_2(COO)_2$/MgO (sol-gel) (act. 673 K)	1.23
Ru + $Cs_2(COO)_2$/MgO (sol-gel) (act. 623 K)	1.48	Ru/MgO (sol-gel) (act. 723 K)	0.00

shows peaks assignable to MgO periclase, while in the trace of the sample activated up to 673 K (b) two small enlarged peaks appear ($2\theta = 38.7°$ and $59.2°$), assignable to Ru metal particles, whose dimensions, although absolutely small, evidently grew from 623 to 673 K. The same peaks also appear in the XRD spectrum (c) of the unpromoted Ru/MgO catalyst activated up to 723 K.

As further evidence, the TEM image of the same catalyst activated up to 623 K (figure 10) shows very small (about 4–5 nm) and well-dispersed Ru particles in the supporting gel.

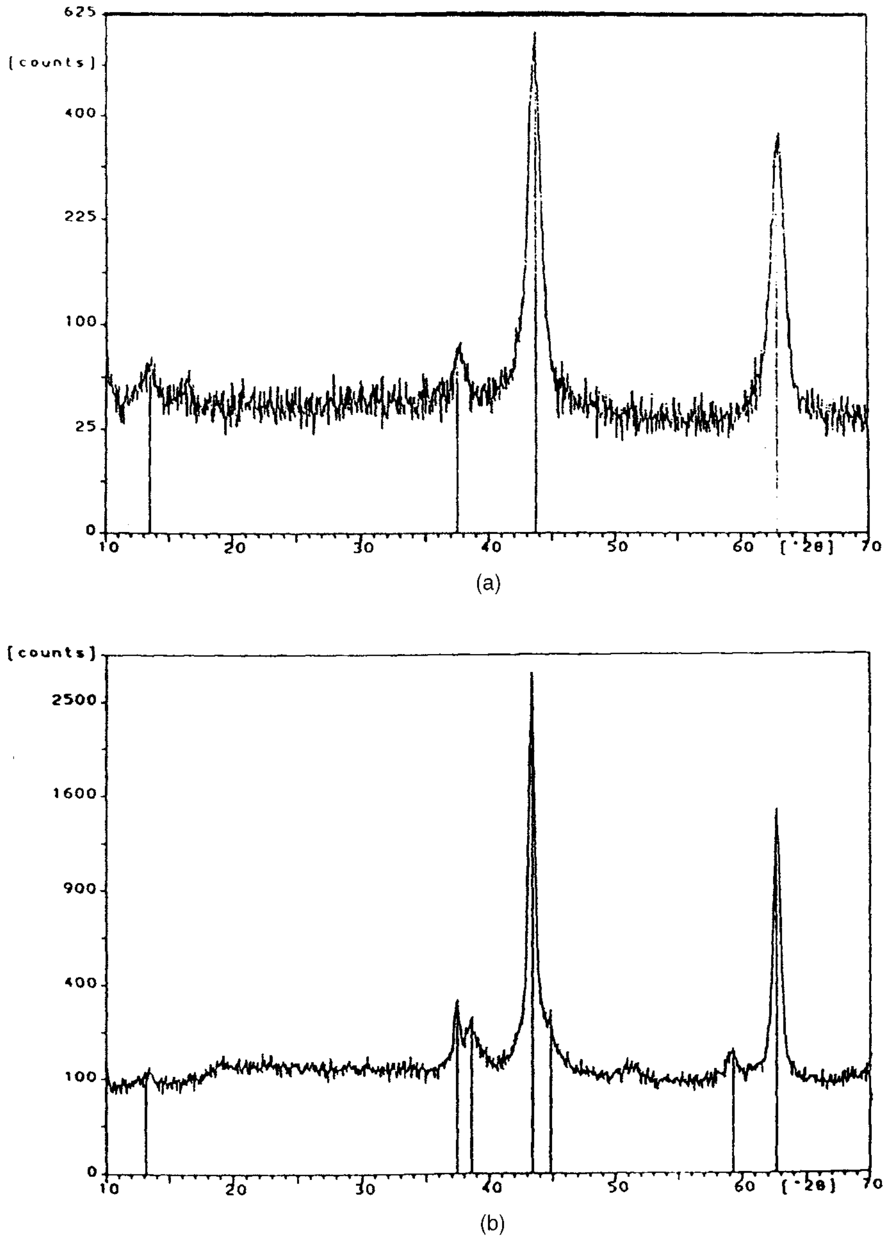


Figure 9. XRD spectra of (a) Ru-Cs/MgO catalyst, sol-gel prepared from $Cs_2(COO)_2$ activated up to 623 K; (b) the same catalyst activated up to 673 K; (c) Ru/MgO activated up to 723 K.

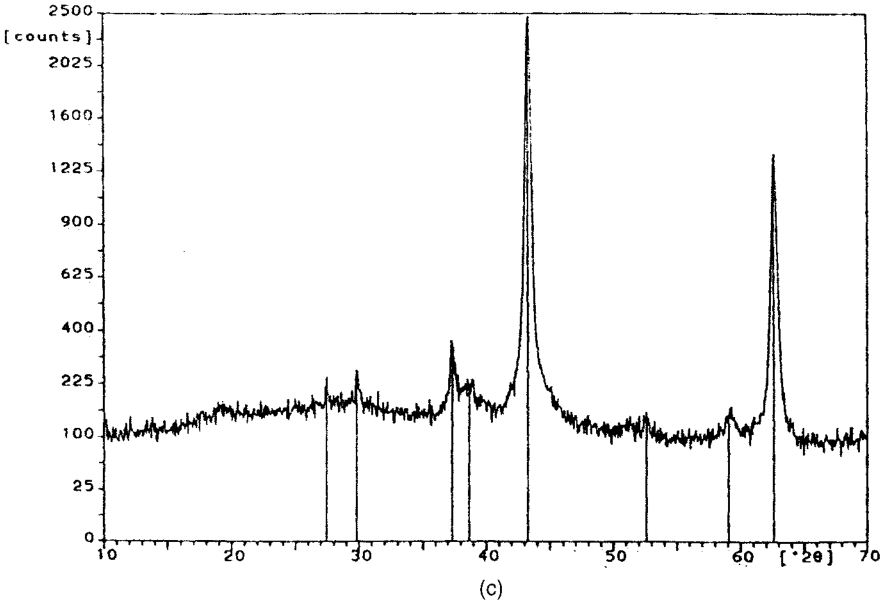


Figure 9. Continued.

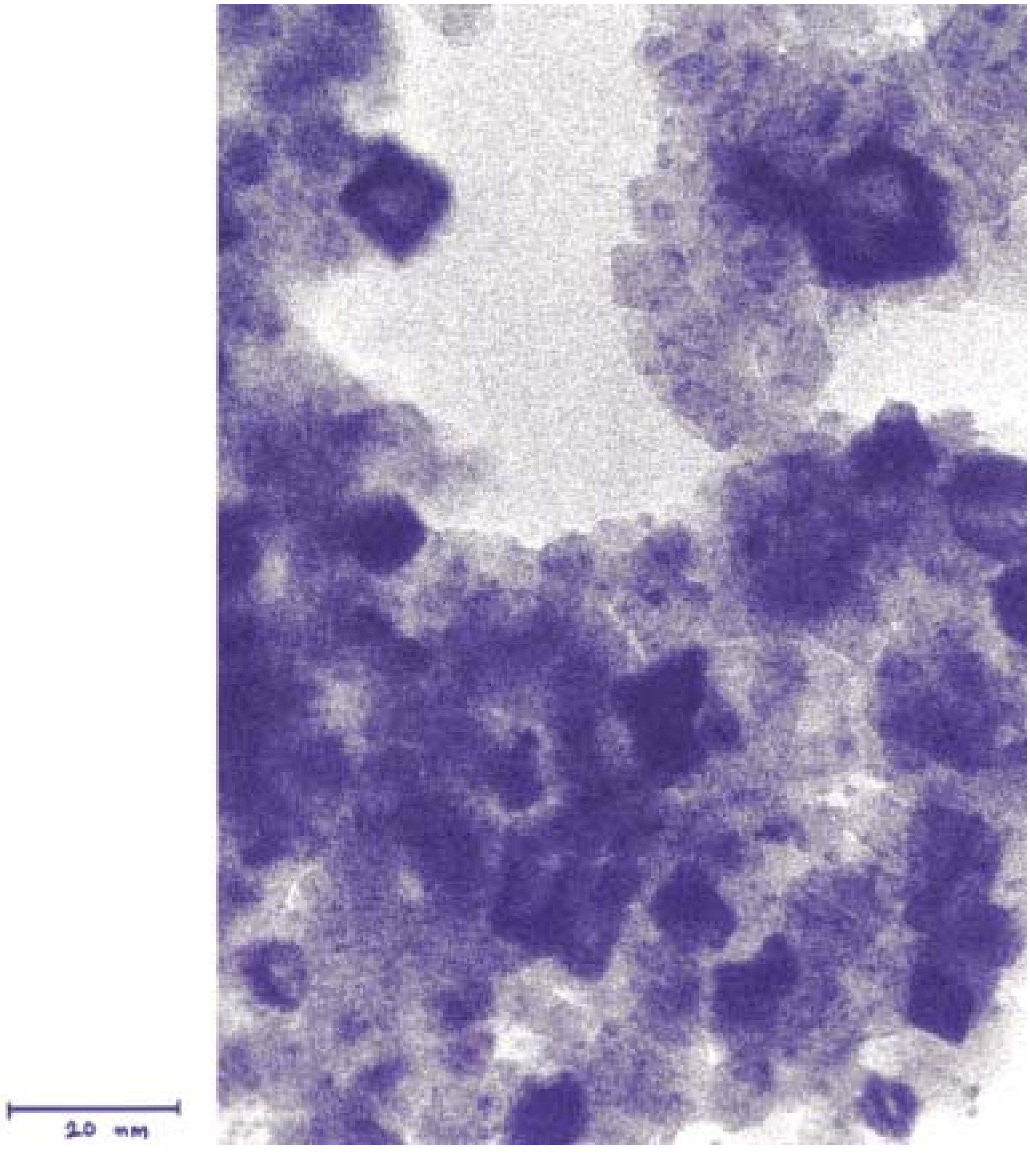


Figure 10. TEM image of the Ru-Cs/MgO catalyst, sol-gel prepared from $Cs_2(COO)_2$ activated up to 623 K.

4. Conclusions

A new method of preparation of a Ru-Cs/MgO catalyst, based on a sol-gel single-step procedure from $Ru_3(CO)_{12}$, $Mg(OEt)_2$ and a cesium compound, has been described, which allowed the chemisorption of Ru precursor on the inorganic support and the obtainment after the activation and reduction stages of very small and well-dispersed metal particles.

The sol-gel prepared Ru-Cs/MgO catalyst was much more active than the analogous one, prepared by impregnation of MgO, indicated from recent literature [1] as the best catalyst in the ammonia synthesis from $N_2 + 3H_2$, also at high pressure.

The best results were obtained with the sol-gel-prepared catalysts when using $Cs_2(COO)_2$, rather than Cs_2CO_3 or CsN_3, as Cs precursor.

Acknowledgments

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