

THERMO-CHEMICAL STABILITY OF RHODIUM-BASED CATALYSTS FOR CONVERSION OF TAR INTO SYNGAS

P. Ammendola*, L. Lisi*, G. Ruoppolo*

paola.ammendola@irc.cnr.it

*Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80 Napoli

Abstract

The thermal and chemical stability of alumina supported catalysts (Rh/Al₂O₃, LaCoO₃/Al₂O₃, Rh-LaCoO₃/Al₂O₃) have been investigated by performing cycles of tar conversion at 700°C followed by regeneration of the catalyst by oxidation of coke deposited on the surface up to 800°C. Structural and chemical modifications undergone by the catalysts upon conversion/regeneration cycles have been studied by BET and TPR/TPO analyses. The catalysts containing rhodium are highly stable maintaining the original performance and chemical properties of the fresh sample also after several cycles, dispersion of rhodium on Al₂O₃ surface being sufficiently preserved also at 800°C. The presence of LaCoO₃ layer further prevents rhodium aggregation. On the contrary, LaCoO₃/Al₂O₃ catalyst undergoes a partial deactivation after the first cycles related to the irreversible migration of cobalt into the alumina lattice.

Introduction

In the last decade the depletion of fossil fuels shifted the attention of the scientific community towards renewable sources. Biomass represents one of the most available renewable fuels which can be converted into bio-oil or syngas [1,2]. A clean syngas can be produced by biomass gasification for energy purpose or production of fine chemicals provided that a suitable conditioning is operated. Indeed, the biomass gasification at 700-900°C produces, in addition to a gas containing H₂, CO, CO₂ and light hydrocarbons, a solid residue (char) and a mixture of condensable hydrocarbons, mostly aromatics, called tar [1,2]. Condensation of tar in downstream pipes and filters represent a severe drawback and must be necessarily avoided.

The more common methods for removing tars include physical methods, such as filtration, or chemical processes, such as thermal cracking or catalytic conversion. Filtration generally requires multiple expensive downstream unit operations, while thermal cracking must be carried out at very high temperatures. Catalytic conversion of tars can be operated at significantly lower temperatures (650-850°C) and, at the present, is the best technology to remove tar.

A large variety of catalysts have been proposed ranging from natural materials as dolomite or olivine to synthetic catalysts [2-4]. More recently, Rh-based catalysts have been proposed as highly performing catalysts for tar conversion [5,6] inhibiting coke formation and showing a very good resistance to poisoning by sulfur compounds, often present in the biomass [7].

Nevertheless, the activity is not the only parameter to be considered, the catalyst life-time being important as well. Indeed, during its use the catalyst undergoes several redox and thermal cycles and, consequently, permanent or reversible deactivation can occur.

In order to investigate the thermal and chemical stability of the alumina supported rhodium-based catalysts cycles of tar conversion followed by regeneration of the temporarily deactivated catalyst due to coke deposition have been carried out. The possible modifications of the structural and redox properties of both LaCoO_3 and Rh upon repeated cycles have been also studied by BET and TPR/TPO techniques and related to the performance after each cycle.

Experimental

Catalysts preparation

Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, >99.9%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka, $\geq 99\%$) to obtain 20 wt% LaCoO_3 were dissolved in a water solution containing the alumina support (La-stabilized $\gamma\text{-Al}_2\text{O}_3$ Puralox SCF140-L3, SASOL). The solution was completely evaporated and then the powder sample dried for 2 h at 120°C and calcined in flowing air for 3 h at 800°C . A fraction of calcined $\text{LaCoO}_3/\text{Al}_2\text{O}_3$ powder was impregnated with a $\text{Rh}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Riedel-de-Haën) solution using an amount of rhodium corresponding to 1% wt, then drying and calcination were repeated. A 1 wt% $\text{Rh}/\text{Al}_2\text{O}_3$ was prepared impregnating the alumina support using the same rhodium precursor.

Catalyst characterization

Rhodium and cobalt contents were quantitatively determined using an ICP-MS Agilent 7500 instrument. Catalyst surface area measurements were carried out according to BET method by N_2 adsorption at 77K with a Quantachrome Autosorb 1-C analyzer.

H_2 TPR and TPO experiments were carried out with a Micromeritics Autochem II TPD/TPR analyzer. Approximately 100 mg of catalyst was reduced with a 2% H_2/Ar mixture ($50 \text{ Ncm}^3 \cdot \text{min}^{-1}$) at $10^\circ\text{C} \cdot \text{min}^{-1}$ up to 800°C after a 1 h in-situ pre-treatment in air at 800°C . After the first TPR experiment the sample was re-oxidized under 0.5% O_2/He mixture heating at $10^\circ\text{C} \cdot \text{min}^{-1}$ up to 800°C . The TPR/TPO cycle was repeated according to this procedure until TPR profiles were superimposable.

Catalytic tests

The experimental set-up consisted of two fixed bed quartz reactors heated independently. The biomass sample (0.5 g of maple wood chips with the following proximate composition: 8.9%wt moisture, 74.6%wt volatiles, 15.9%wt fixed

carbon, 0.6%wt ash, and the following chemical composition estimated on dry basis: 46.28%wt C, 5.56%wt H, 47.52%wt O, 0%wt N) was heated up in the first furnace under pure N₂ (12 NI·h⁻¹). The gaseous and condensable products formed during biomass pyrolysis in the first reactor passed through the second reactor containing the catalyst (0.50 g) at 700°C and then through a two stage-condenser to collect heavier tars at room temperature and lighter ones at -20°C, following the CEN/TS 15439 (2006) procedure. The permanent gases were sent to a micro-gas-chromatograph (Agilent 3000A), equipped with four different independent channels and a TCD. The lines between the first and second reactor as well as between the second reactor and the tars condensation train were heated (300-400°C) to avoid the condensation of tarry compounds.

The sampling train was weighed before and after each experiment for the quantitative evaluation of the tars yield.

At the end of each experiment the amount of coke deposited on the catalyst was determined by oxidation of the material at 800°C. The amount of released CO₂ provided the stoichiometric amount of coke formed during the previous catalytic tar conversion experiment and the regeneration of the catalyst surface as well.

Catalytic activity was thus estimated as the difference between the yields and type of gas, liquid and solid products obtained with the different catalysts. For all experiments the mass balance was closed with a maximum error of ±10% wt.

Results and discussion

The actual metals content are close to the nominal one. The deposition of rhodium results in a slight reduction of the surface area of the alumina support whereas the deposition of LaCoO₃ causes a larger decrease. No significant effect on BET surface areas of either conversion/regeneration or TPR/TPO cycles were observed for all samples thus showing a good structural stability.

TPR/TPO cycles were performed in order to reproduce the redox cycles the catalyst undergoes. Indeed, the catalyst is exposed to a reducing atmosphere under the tar conversion reaction (the oxygen is just that of the biomass pyrolysis products in addition to that of the supported metal oxide) and to an oxidizing atmosphere under regeneration conditions when oxygen oxidizes coke on the surface and, in case, re-oxidize the alumina-dispersed metal.

In Figures 1-2 TPR profiles of LaCoO₃/Al₂O₃, Rh/Al₂O₃ and Rh-LaCoO₃/Al₂O₃ are reported. In each figure the TPR analysis carried out on the fresh sample (1st TPR) is compared with the following ones (2nd and 3rd TPR) carried out after a TPO to re-oxidize the sample. The first TPR profile of LaCoO₃/Al₂O₃ (Fig. 1) has the typical features of perovskite-like oxide dispersed on alumina [5], showing the two peaks associable to the reduction of cobalt from +3 to +2 and +2 to 0 respectively. The H₂ uptake, below the theoretical value for reduction of all Co³⁺ to metallic cobalt, suggests that a significant fraction of the transition metal is not available for the catalytic reaction [6]. The second TPR performed after a TPO up to 800°C shows a reduction of these two peaks balanced by the appearance of a new peak at

higher temperature typical of cobalt diffused in the alumina matrix forming aluminate (CoAl_2O_4) [5]. The further TPO/TPR cycle does not significantly modifies the profile suggesting that the cobalt migration basically takes place in the first cycle.

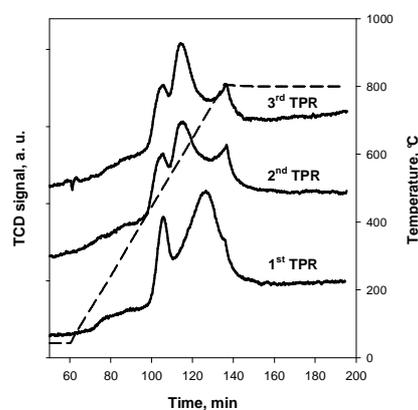


Figure 1. TPR profiles of $\text{LaCoO}_3/\text{Al}_2\text{O}_3$ catalyst.

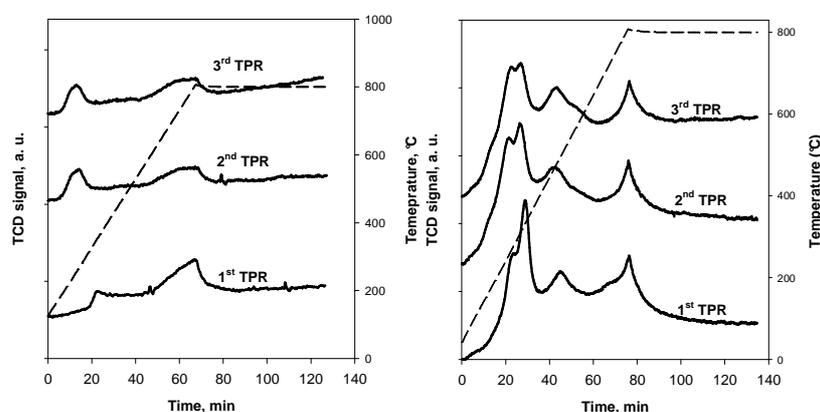


Figure 2. TPR profiles of $\text{Rh}/\text{Al}_2\text{O}_3$ (left) and $\text{Rh-LaCoO}_3/\text{Al}_2\text{O}_3$ (right) catalysts.

The first TPR cycle of $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst (Fig. 2 left) shows two signals related to surface RhO_x and to RhAlO_x [5]. The following TPR/TPO cycles result in a shift towards lower temperature of the signal attributed to RhO_x surface species which also increases in intensity. The total H_2 uptake corresponds to the complete reduction of rhodium from +3 to 0 and does not significantly changes in the subsequent TPR cycles.

The TPR profiles of $\text{Rh-LaCoO}_3/\text{Al}_2\text{O}_3$ catalyst (Fig. 2 right) show a medium temperature peak corresponding to the reduction of cobalt in the perovskite-like oxide and a high temperature peak related to the reduction of cobalt aluminate. The signal at low temperature, associated to highly dispersed rhodium species [5], is

much higher than that observed for Rh/Al₂O₃ due to a barrier effect of the LaCoO₃ layer which inhibits rhodium migration. The comparison of the first TPR with the following ones does not evidence significant differences of the medium and high temperature peaks but a slight modification of the low temperature signal. This peak is clearly composed by two contributions which were attributed to aggregate rhodium species (lower temperature) and isolated rhodium species (higher temperature) respectively. The comparison of the TPR profiles suggests that the TPR/TPO cycles promote the aggregation of the surface species.

In Table 1 the results of all catalytic tests are reported as solid (char and coke), liquid and gas yields. All catalysts are able to effectively convert tar mainly into gaseous species leaving a low fraction of carbonaceous compounds on the catalyst surface as coke. The LaCoO₃/Al₂O₃ catalyst, providing performance comparable to that of the Rh containing catalysts in the first cycle, clearly shows a considerable activity loss in the second cycle which, however, is not significantly further reduced in the third cycle. On the other hand, when rhodium is present in the catalyst formulation deactivation after the first conversion cycle is definitely less important. For both Rh containing samples just a limited decrease of gas yield was observed after the first cycle balanced by a slight increase of coke yield. No liquids were collected neither light hydrocarbons were detected in the gas phase for both Rh-based catalysts in all cycles experienced. Moreover, stable performance was obtained for the Rh-LaCoO₃/Al₂O₃ catalyst up to six cycles showing that the little modification the material underwent after the first cycle, does not increase further.

Table 1. Solid, liquid and gas yields in the cycles for all Al₂O₃-supported catalysts.

catalyst	cycle	solid yield (wt%)		liquid yield (wt%)	gas yield (wt%)
		char	coke		
LaCoO ₃	1 st	18.3	3.6	-	75.9
	2 nd	18.0	5.6	11.9	56.8
	3 rd	18.2	5.1	12.4	55.9
Rh	1 st	16.5	2.0	-	76.5
	2 nd	18.6	2.7	-	71.7
	3 rd	18.6	2.9	-	72.3
Rh-LaCoO ₃	1 st	17.0	1.3	-	75.0
	2 nd	17.0	1.7	-	72.4
	3 rd	17.2	2.1	-	71.0

Both H₂ and CO yields are reduced after the first cycle for the LaCoO₃/Al₂O₃ catalyst, CO₂ is quite constant in all cycle whilst the amount of light hydrocarbons increases. This is an indication that sites active for reforming are partly deactivated upon the first conversion/regeneration treatment whereas cracking still occurs.

The stable performance of Rh-based catalysts are also shown by the rather constant H₂ and CO yields evaluated after the first cycle. However, the Rh- LaCoO₃/Al₂O₃ catalyst is the most stable and although it contains a higher fraction of larger Rh particles as fresh compared to the sample not containing LaCoO₃, the dispersion of the noble metal into the matrix of the perovskite-like oxide limits its further aggregation thus stabilizing the catalyst towards thermal and redox cycles.

Conclusions

The thermo-chemical stability of Rh/Al₂O₃, LaCoO₃/Al₂O₃, Rh-LaCoO₃/Al₂O₃ catalysts has been investigated in reforming of tar from biomass decomposition. Repeated cycles of tar conversion at 700°C followed by regeneration of the catalyst by oxidation of coke deposited on the surface up to 800°C were carried out in order to test the catalyst life-time. All catalysts show a good structural stability, however, those containing rhodium also show a satisfactory physic-chemical stability preserving the original performance and chemical properties of the fresh sample also after several cycles. In addition, rhodium aggregation is prevented thanks to the stabilizing effect the perovskite-like oxide.

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References

- [1] Yung M. M., Jablonski W. S., Magrini-Bair K. A., “Review of catalytic conditioning of biomass-derived syngas”, *Energy & Fuels* 23: 1874 (2009)
- [2] Dayton D., “A review of the literature on catalytic biomass tar destruction”, Milestone completion report, NREL/TP-510-32815 (2002)
- [3] Kuhn J., Zhao Z., Felix L. G., Rachid B., Slimane R. B., Choi C. W., Ozkan U. S., “Olivine catalysts for methane- and tar-steam reforming”, *Appl. Catal. B: Environmental* 81: 14-26 (2008)
- [4] Wang L., Li D., Koike M., Kosoa S., Nakagawa Y., Xud Y., Tomishige K., “Catalytic performance and characterization of Ni-Fe catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas”, *Appl. Catal. A: General* 392: 248-255 (2011)
- [5] Ammendola P., Lisi L., Piriou B., Ruoppolo G., “Rh-perovskite catalysts for conversion of tar from biomass pyrolysis”, *Chem. Eng. J.* 154: 361-368 (2009)
- [6] Ammendola P., Piriou B., Lisi L., Ruoppolo G., Chirone R., Russo, G., “Dual bed reactor for the study of catalytic biomass tars conversion”, *Exper. Therm. Fluid Sci.* 34: 269-274 (2010)
- [7] Ammendola P., Cammisa E., Chirone R., Lisi L., Ruoppolo G., “Effect of sulphur on the performance of Rh-LaCoO₃ based catalyst for tar conversion to syngas”, *Appl. Catal. B: Environmental* 113–114: 11-18 (2012)