**H2 AND/OR C3H6 ASSISTED SELECTIVE CATALYTIC REDUCTION OF NOx OVER Ir/ACZ CATALYSTS**

THEODORIDIS G.I.1, CHARISIOU N.D.1, DOUVARTZIDES S.2, TSIOTSIAS A.I.1, DROSOU C.3, YENTEKAKIS I.V.3,\*, GOULA M.A.1,\*

1Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC), Department of Chemical Engineering, University of Western Macedonia, 50100, Kozani, Greece,

2Department of Mechanical Engineering, University of Western Macedonia, 50100, Kozani, Greece,

3Laboratory of Physical Chemistry and Chemical Processes, School of Environmental Engineering, Technical University of Crete, 73100 Chania, Greece

\*Corresponding Authors: M.A. Goula (mgoula@uowm.gr); I.V. Yentekakis (yyentek@isc.tuc.gr)

SUMMARY: Selective Catalytic Reduction (SCR) is widely considered as one of the most effective aftertreatment technologies for the control of the emissions of nitrogen oxides (NOx) in the effluents of lean combustion. In the present work, the SCR of NO was investigated at the temperature range of 150-500oC over low loading (1 wt.%) Ir catalysts based on Al2O3-CeO2-ZrO2 (ACZ) supports with different Al-Ce-Zr molar compositions. The study examined three reaction schemes (NO + C3H6 + O2 (R#1), NO + H2 + O2 (R#2) and NO + C3H6 + H2 + O2 (R#3)) over two groups of catalysts, one with ACZ supports synthesized by a hydrothermal method and another with the ACZ supports synthesized by co-precipitation. The results showed that the maximum NO conversion was attained over the Ir-ACZ (C:Z=75:25) hydrothermal catalyst and the Ir-ACZ (C:Z=50:50) co-precipitated catalyst regardless of the reducing agent in the reaction mixture. An increase of the O2 concentration from 2% to 5% increased the conversion of NO, but led to a decline in the yield towards N2, for both catalysts.

1. INTRODUCTION

The combustion of fossil fuels in both transportation and industrial applications is known to produce significant emissions of nitrogen oxides, i.e., NOx (NO and NO2) [1-4]. Selective Catalytic Reduction (SCR) is widely considered as one of the most effective aftertreatment technologies for the control of nitrogen oxides in the combustion effluents [5-8]. The method intends the heterogeneous catalytic reduction of NOx in the presence of a homogeneous reducing agent and is particularly suitable for oxygen-rich effluents coming from lean combustion applications, as it is the case in residential and industrial burners or in vehicular diesel engines [9-12]. The present experimental work investigates the SCR of NOx over Ir/Al2O3-CeO2-ZrO2(ACZ) catalysts prepared by two different methods (hydrothermal and co-precipitation) and in the presence of three alternative reducing agents: C3H6 (R#1), H2 (R#2) and C3H6 + H2 (R#3).

2. EXPERIMENTAL

**2.1 Catalyst preparation**

The SCR of NO was investigated at the temperature range of 150-500oC over low loading (1 wt.%) Ir catalyst dispersed on Al2O3-CeO2-ZrO2 (ACZ) supports with different Al-Ce-Zr molar compositions. Two different groups of catalysts were prepared. In the first, the ACZ supports were synthesised using a hydrothermal synthesis method at 100 oC for 20 h while in the second the ACZ supports were synthesized using the typical co-precipitation method at room temperature and under a controlled pH-value equal to 9-10. The precursors used in both methods were Al(NO3)3·9H2O, Ce(NO3)3·6H2O and Zr(NO3)2·H2O nitric salts, which were diluted in distilled water with the appropriate quantities to provide a final ACZ support comprised of 60 wt.% Al2O3 and 40 wt.% CeO2-ZrO2. The C:Z molar ratio was designed to be 0.75:0.25, 0.5:0.5 and 0.25:0.75. Then, the obtained precipitates were dried at 110 oC overnight and the samples were calcined at 800 oC for 2 h. The as prepared ACZ mixed oxides were impregnated by IrCl2 solution with the appropriate amount of Ir in order to obtain an Ir loading of 1wt.%. The resulting suspensions were dried at 110 oC overnight and then directly reduced at 400 oC under 25 % H2/Ar flow for 3 h to avoid the formation of large Ir crystallites.

**2.2 Catalytic tests**

Ir/ACZ (75-25), Ir/ACZ (50-50), Ir/ACZ (25-75) and Ir/Al2O3 catalysts were tested at the same experimental conditions for all the reducing agents. Τhe initial gas mixture composition was 1000 ppm or 2000 ppm NO, 1000 ppm or 2000 ppm C3H6 (when appropriate), 1000 ppm or 2000 ppm H2 (when appropriate), 2 or 5% O2 and inert Ar as balance at 1 bar. For each experiment 0.18 g of catalyst was used and was positioned in a fixed bed quartz tubular flow reactor. Then experiments were carried out keeping the gas hourly space velocity equal to 100,000 h−1.

3. RESULTS AND DISCUSSION

**3.1 Selective catalytic reduction with C3H6 (reaction scheme R#1)**

Initially, the effect of the C:Z molar composition was examined for the catalysts prepared with the hydrothermal method using C3H6 as the reducing agent (1000 ppm) and in presence of 2% O2 and 1000 ppm NO in the reacting mixture. As shown in Figure 1a, the maximum obtained NO conversion was achieved at 360oC, and followed the order: Ir-ACZ(75-25) 35% > Ir-ACZ(50-50) 32% $≈$ Ir-ACZ(25-75) 32% > Ir-Al2O3 23% (for this latter catalyst the value was recorded at 380oC). The yield towards N2 (Figure 1b), at 300oC, followed the order Ir-ACZ(25-75) 16% > Ir-ACZ(75-25) 14% > Ir-ACZ(50-50) 10% > Ir-Al2O3 3%. Over 400oC, the yield to N2 rises sharply for all catalysts, apart from the unmodified one.

Using the Ir-ACZ(75-25),which exhibited the best performance in this experimental series, two more experiments were conducted, with different reactant concentrations: a) 5% O2 and 1000 ppm NO (1000 ppm C3H6), and b) 5% O2 and 2000 ppm NO (2000 ppm C3H6). From the results presented herein (Figure 1c), the increase of O2 content from 2% to 5% led to an increase of NO conversion from 35% to 47% (at 360oC). However, when increasing the concentration of NO to 2000 ppm (using 5% O2), NO conversion dropped to 38% (Figure 1c). In both these cases, the yield to N2 was about 5% at 300oC (Figure 1d).

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** | **(d)** |

**Figure 1.** Hydrothermal catalysts: (a) NO conversion, and (b) Yield of N2 *(for both (a) and (b) reaction conditions: 1000 ppm NO, 1000ppm C3H6, 2% O2).* Ir-ACZ(75-25): (c) NO conversion, and (d) Yield of N2 *(for both (c) and (d) reaction conditions: 1000 ppm NO (1000ppm C3H6) vs 2000ppm NO (2000 ppm C3H6), 5% O2)*.

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** | **(d)** |

**Figure 2:** Co-precipitation catalysts: (a) NO conversion, and (b) Yield of N2 *(for both (a) and (b) reaction conditions: 1000 ppm NO, 1000 ppm C3H6, 2% O2).* Ir-ACZ(75-25): (c) NO conversion, and (d) Yield of N2 *(for both (c) and (d) reaction conditions: 1000 ppm NO (1000 ppm C3H6) vs 2000ppm NO (2000 ppm C3H6), 5% O2)*.

In the second set of experiments the effect of the C:Z molar composition was examined for the catalysts prepared through co-precipitation using C3H6 as the reducing agent (1000 ppm) and in the presence of 2% O2 and 1000 ppm NO in the reactants. As shown in Figure 2a, the maximum obtained NO conversion, at 360oC, followed the order Ir-ACZ(50-50) 56% > Ir-ACZ(75-25) 31% > Ir- ACZ(25-75) 18%. Interestingly, conversion was rather stable between 400-500oC. The yield towards N2 (Figure 2b) showed a first peak around 300oC, following the order Ir-ACZ(50-50) 43% > Ir-ACZ(25-75) 11% > Ir-ACZ(75- 25) 7%. Over 350oC, YN2 rose monotonically up to the end of the experiment at 500oC.

Similarly to the experimental protocol followed above, the catalyst that showed the highest NO conversion (i.e., Ir-ACZ(50-50)) was further tested with different reactant concentrations: a) 5% O2 and 1000 ppm NO (1000 ppm C3H6), and b) 5% O2 and 2000 ppm NO (2000 ppm C3H6). As can be seen in Figure 2c, an increase of O2 concentration from 2% to 5% increased the NO conversion at 61% at 360oC (from 56%), while the yield of N2 (Figure 2d) declined slightly to about 38% (at 300oC). With the reactants at 5% O2 and 2000 ppm NO, the NO conversion was about 38% (at 360oC) while the N2 yield again showed a first peak at 300oC (23%), declined somewhat between 300-400oC and rose again after this temperature.

**3.2 Selective catalytic reduction with H2 (reaction scheme R#2)**

In this set of experiments, C3H6 was replaced as reducing agent by H2 and the results are presented in the comparative manner shown above, i.e., first the results obtained using the catalysts prepared via the hydrothermal method, followed by the results obtained using the catalysts synthesised using the co-precipitation technique.

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** | **(d)** |

**Figure 3:** Hydrothermal catalysts: (a) NO conversion, and (b) Yield of NO2 *(for both (a) and (b) reaction conditions: 1000 ppm NO, 1000 ppm H2, 2% O2).* Ir-ACZ(75-25): (c) NO conversion, and (d) Yield of NO2 *(for both (c) and (d) reaction conditions: 1000 ppm NO (1000 ppm H2) vs 2000 ppm NO (2000 ppm H2), 5% O2)*.

Examining first the catalysts prepared with the hydrothermal method, and in the presence of 2% O2 and 1000 ppm NO (1000 ppm H2) in the reacting mixture, the maximum obtained NO conversion (Figure 3a) for all Ir-ACZ catalysts was about 35% at 360oC; only the Ir-Al2O3 showed somewhat lower NO conversion (29%). Also, for all catalysts the yield towards N2 was negligible; apparently, NO was converted almost entirely to NO2 (Figure 3b). Similarly to the experimental work presented above, further experiments were carried out using the Ir-ACZ(75-25), keeping constant the concentration of NO at 1000 ppm (1000 ppm H2), and increasing the O2 content from 2% to 5%. The results once again show that NO conversion increased to 44% (at 360oC), but as above, an increase in the concentration of NO in the feed to 2000 ppm (2000 ppm H2) lead to a decrease in the conversion of NO to about 20% (keeping the O2 content in the feed at 5%) (Figure 3c). For both cases, the yield to N2 was negligible and NO seems to have been converted to NO2 (Figure 3d).

Figure 4 illustrates the results for the catalysts prepared with co-precipitation using H2 (1000 ppm) as the reducing agent, in the presence of 2% O2 and 1000 ppm NO in the reacting mixture. As shown, the maximum obtained NO conversion (Figure 4a) was achieved at different temperatures for each catalyst, as follows: Ir-ACZ(50-50) 47% (400oC), Ir-ACZ(75-25) 37% (360oC), and Ir-ACZ(25-75) 26% (380oC). It is also worth mentioning that the Ir-ACZ(50-50) catalyst exhibited very high and stable NO conversion between 400-500oC. Most interestingly, the Ir-ACZ(50-50) was the only one that yielded N2, showing steadily rising values for the duration of the experiment (maximum YN2 41% at 500oC) (Figure 4b).

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** | **(d)** |

**Figure 4:** Co-precipitation catalysts: (a) NO conversion, and (b) Yield of N2 *(for both (a) and (b) reaction conditions: 1000 ppm NO, 1000 ppm H2, 2% O2).* Ir-ACZ(75-25): (c) NO conversion, and (d) Yield of N2 *(for both (c) and (d) reaction conditions: 1000 ppm NO (1000 ppm H2) vs 2000 ppm NO (200 0ppm H2), 5% O2)*.

For this later catalyst (i.e., Ir-ACZ(50-50)), keeping constant the concentration of NO at 1000 ppm (1000 ppm H2), an increase of O2 concentration from 2% to 5% did not change the maximum NO conversion (Figure 4c) but it declined the yield of N2 to about 21% (at 500oC) (Figure 4d). By increasing the concentrations of the reactants at 5% O2 and 2000 ppm NO (2000 ppm H2), the maximum NO conversion was about 21% (360oC) while the maximum N2 yield dropped to about 3% at 500oC.

**3.3 Selective catalytic reduction with C3H6 + H2 (reaction scheme R#3)**

The final set of experiments (reaction scheme R#3) was carried out using both C3H6 (1000 ppm) and H2 (1000 ppm) as reducing agents; again, initially, the reactant mixture contained 2% O2 and 1000 ppm NO. Turning our attention first to the results obtained using the catalysts prepared via hydrothermal synthesis, it is obvious that NO conversion (Figure 5a) presents, for all catalysts, two peaks; the first is recorded approximately at 275oC, while the higher temperature peak appears between 400-460oC. For this latter peak, NO conversion was recorded at Ir-ACZ(75-25) 42% (420oC), Ir-ACZ(50-50) 30% (380oC), Ir-ACZ(25-75) 35% (460oC), and Ir-Al2O3 31% (420oC). The yield towards N2 (Figure 5b) also shows the presence of a low and a high temperature peaks, around 260oC for the former and between 450-500oC for the latter. At 460oC, YN2 took the following values: Ir-ACZ(75-25) 31%, Ir-ACZ(50-50) 18%, Ir-ACZ(25-75) 24%, and Ir-Al2O3 19%.

Using the Ir-ACZ(75-25), the increase of O2 concentration to 5% (1000 ppm NO, 1000 ppm C3H6, 1000 ppm H2) virtually eliminated the low temperature NO conversion peak and sharpened the high temperature one (Figure 5c). Thus, the maximum NO conversion was achieved at 360oC (about 60oC lower that previously), at 46% (slightly larger value). The yield of N2 followed a similar trend, obtaining a value of 11%, at 460oC (Figure 5d). With the reactants at 5% O2 and 2000 ppm NO (1000 ppm C3H6, 1000 ppm H2) the maximum NO conversion was about 23% at 360oC, while the maximum N2 yield was about 16% (at 460oC).

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** | **(d)** |

**Figure 5:** Hydrothermal catalysts: (a) NO conversion, and (b) Yield of N2 *(for both (a) and (b) reaction conditions: 1000 ppm NO, 1000 ppm C3H6, 1000 ppm H2,2% O2).* Ir-ACZ(75-25): (c) NO conversion, and (d) Yield of N2 *(for both (c) and (d) reaction conditions: 1000 ppm NO (1000 ppm C3H6, 1000 ppm H2) vs 2000 ppm NO (2000 ppm C3H6, 2000 ppm H2, 5% O2)*.

Figure 6 illustrates the results for the catalysts prepared with co-precipitation using C3H6 and H2 as reducing agents and in the presence of 2% O2 and 1000 ppm NO in the reacting mixture. As above, a low and a high temperature peak (Figure 6a) are shown for NO conversion, albeit the former is less well defined in comparison to the results obtained for the catalysts prepared for hydrothermal synthesis (Figure 5a). The maximum NO conversion was achieved at 420oC for all catalysts and followed the order Ir-ACZ(50-50) 49% > Ir-ACZ(25-75)  39% > Ir-ACZ(75-25) 32%. Also, the maximum yield of N2 (Figure 6b), at 420oC, followed the order Ir-ACZ(50-50) 42% > Ir-ACZ(25-75) 26% > Ir-ACZ(75-25) 15%. For the Ir-ACZ(50-50), an increase of O2 concentration to 5% led to a decrease in NO conversion (Figure 6c) to 33% and of the yield to N2 (Figure 6d) to about 13% (both values at 420oC). With the reactants at 5% O2 and 2000 ppm NO, the NO conversion was about 37% and the N2 yield was about 23% (both values at 420oC).

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** | **(d)** |

**Figure 6:** Co-precipitation catalysts: (a) NO conversion, and (b) Yield of N2 *(for both (a) and (b) reaction conditions: 1000ppm NO, 1000 ppm C3H6,1000ppm H2, 2% O2).* Ir-ACZ(75-25): (c) NO conversion, and (d) Yield of N2 *(for both (c) and (d) reaction conditions: 1000 ppm NO (1000 ppm C3H6*, *1000 ppm H2) vs 2000ppm NO (2000 ppm C3H6, 2000ppm H2, 5% O2)*.

5. CONCLUSIONS

In the work presented herein, Ir catalysts with a low loading (1 wt.%), supported on Al2O3-CeO2-ZrO2 (ACZ), were tested for the selective catalytic reduction of NO. The supports were prepared using two different synthesis methods, (a) hydrothermal and b) co-precipitation; for each method three different Ce:Zr molar compositions were utilized (75:25, 50:50, and 25:75). The as prepared catalysts were tested in the temperature range of 150-500oC under three reaction schemes: NO + C3H6 + O2 (R#1), NO + H2 + O2 (R#2) and NO + C3H6 + H2 + O2 (R#3). The results showed that the maximum NO conversion was attained over the Ir-ACZ (C:Z=75:25) hydrothermal catalyst and the Ir-ACZ (C:Z=50:50) co-precipitated catalyst regardless of the reducing agent in the reaction mixture. An increase of the O2 concentration from 2% to 5% increased the conversion of NO but led to a decline in the yield towards N2, for both catalysts.

5. ACKNOWLWDGEMENTS

Financial support by the Greek-Chinese bilateral research and innovation cooperation, 2018-2021 program (Project No: T7ΔΚI-00356) is gratefully acknowledged.

**REFERENCES**

1. M.A. Goula, N.D. Charisiou, K.N. Papageridis, A. Delimitis, E. Papista, E. Pachatouridou, E.F. Iliopoulou, G. Marnellos, M. Konsolakis, I.V. Yentekakis. A comparative study of the H2-assisted selective catalytic reduction of nitric oxide by propene over noble metal (Pt, Pd, Ir)/γ-Al2O3 catalysts. *Journal of Environmental Chemical Engineering* **2016**, *4*, 1629–1641.
2. Z. Gholami, G. Luo, F. Gholami, F. Yang. Recent advances in selective catalytic reduction of NOx by carbon monoxide for flue gas cleaning process: a review. *Catalysis Reviews* **2020**, 68-119.
3. I.V. Yentekakis, V. Tellou, G. Botzolaki, I.A. Rapakousios. A comparative study of the C3H6 + NO + O2, C3H6 + O2 and NO + O2 reactions in excess oxygen over Na-modified Pt/γ-Al2O3 catalysts. *Applied Catalysis B: Environmental* **2005**, 56, 229–239.
4. M. Konsolakis, I.V. Yentekakis. The Reduction of NO by Propene over Ba-Promoted Pt/γ-Al2O3 Catalysts. *Journal of Catalysis* **2001**, 198, 142–150.
5. E. Papista, E. Pachatouridou, M. A. Goula, G. E. Marnellos, E. Iliopoulou, M. Konsolakis, I. V. Yentekakis. Effect of Alkali Promoters (K) on Nitrous Oxide Abatement Over Ir/Al2O3 Catalysts. *Top Catal.* **2016**, 59, 1020–1027.
6. H. Hamada, M. Haneda. A review of selective catalytic reduction of nitrogen oxides with hydrogen and carbon monoxide. *Applied Catalysis A: General* **2012**, 421– 422, 1– 13.
7. A. Väliheikki, K. C. Petallidou, C. M. Kalamaras, T. Kolli, M. Huuhtanen, T. Maunula, R. L. Keiski, Angelos M. Efstathiou. Selective catalytic reduction of NOx by hydrogen (H2-SCR) on WOx-promoted CezZr1-zO2 solids. *Applied Catalysis B: Environmental* **2014**, 156–157, 72–83.
8. C. Yin, L. Wang, S. Rivillon, A. J. Shih, R.T. Yang. SCR of Nitric Oxide by Hydrogen over Pd and Ir Based Catalysts with Different Supports. *Catal Lett.* **2015**, 145, 1491–1499.
9. M. Ogura, A. Kawamura, M. Matsukata, E. Kikuchi. Catalytic Activity of Ir for NO-CO Reaction in the Presence of SO2 and Excess Oxygen. *Chemistry Letters* **2000**, 29, 2, 146-147.
10. T. Yoshinari, K. Sato, M. Haneda, Y. Kintaichi, H. Hamada. Positive effect of coexisting SO2 on the activity of supported iridium catalysts for NO reduction in the presence of oxygen. *Applied Catalysis B: Environmental* **2003**, 41, 157–169.
11. A. Wang, L. Ma, Y. Cong, T. Zhang, D. Liang. Unique properties of Ir/ZSM-5 catalyst for NO reduction with CO in the presence of excess oxygen. *Applied Catalysis B: Environmental* **2003**, 40, 319–329.
12. M. Konsolakis, I.V. Yentekakis, A. Palermo, R.M. Lambert. Optimal promotion by rubidium of the CO + NO reaction over Pt/γ-Al2O3 catalysts. *Applied Catalysis B: Environmental* **2001**, 33, 293–302.