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# High Zr-loaded SBA-15 cobalt catalyst for efficient NOx reduction in lean-burn exhaust

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Graphical abstract

### Highlights

- High Zr-loaded SBA-15 with a direct-post synthesis method was achieved.
- Non-noble metal-based catalyst was developed by doping cobalt on ZrSBADP2.
- The highest C<sub>3</sub>H<sub>8</sub>-SCR activity was achieved over Co<sub>2</sub>/ZrSBADP<sub>2</sub>.
- A high N<sub>2</sub> yield (70 %) was obtained in the presence of water vapor at 350°C.
- The catalyst structure was stable in the extreme prolonged reaction conditions.

### Abstract

A high Zr-loaded SBA-15 mesoporous material with high surface area, well-ordered structure, homogeneous Zr dispersion and high surface acidity has been prepared by a novel direct-post synthesis technique (DP). While maximum Zr loadings of 5.1 wt% and 16.7 wt% have been achieved in direct and post synthesis methods, respectively, the support synthesized by the DP method (ZrSBADP2) has yielded a Zr loading of 32.1 wt%. Also, a high acidity of 136 µmol. g<sup>-1</sup>, favorable for catalysis reactions, has been reached for ZrSBADP2. The effect of cobalt concentration on the catalyst has also been examined on the NO to N<sub>2</sub> conversion via selective reduction (C<sub>3</sub>H<sub>8</sub>-SCR) with propane. It has been demonstrated that the catalyst with 2 wt% cobalt has shown the highest N<sub>2</sub> yield (70%) at 400°C in the presence of 6 vol% O<sub>2</sub>. The catalyst performance has significantly improved in the presence of water vapor where the N<sub>2</sub> yield increased to 54% and 70% at 300°C and 350°C, respectively, compared with 18% and 34% in the absence of water vapor. Also, at high temperatures ( $\geq$  400°C), the presence of water vapor has not resulted in any decrease in the catalyst performance. The long term stability test has proved that the catalyst structure is retained in extreme prolonged reaction conditions, making it a suitable catalyst for real applications.

### Keywords

Cobalt-based catalysts, NOx reduction, Zr-SBA-15, C<sub>3</sub>H<sub>8</sub>-SCR, Direct-Post synthesis

### **1** Introduction

Growing environmental concerns on NOx emission as a major source for air pollution have driven industrial and governmental sectors to seek for an efficient method to reduce NOx emission from mobile and stationary sources.

Selective catalytic reduction (SCR) of NOx has proved as an effective strategy to convert this poisonous emission into environmental-benign gaseous components. Among many SCR techniques, NOx reduction using hydrocarbon as the reducing agent (HC-SCR) in the lean-burn conditions has been considered as a simple and efficient technique in comparison to other SCR methods, such as NH3-SCR and Urea-SCR. The catalytic system in HC-SCR requires certain properties, such as hydrothermal stability and high surface acidity. Moreover, specific characteristics of the support used for catalyst preparation, such as high surface area and good interaction with active components, will greatly assist the catalyst to exhibit higher activity in the catalytic reactions [1–4].

So far, various types of catalysts including zeolites, metal oxides, transition metal-supported compounds and noble metal-based catalysts, have been developed for HC-SCR [4–6]. Amongst, zeolite-supported cobalt catalyst has exhibited promising results in NO reduction with propane[7–9] that is the main component of unburned hydrocarbons in lean-burn gas, diesel and natural gas-fueled appliances exhausts [10–13]. Shichi et al. [7] reported that Co-MFI zeolite catalyst had 30% and 80% NO conversion at 350 and 400°C, respectively. In another report, 30% and 40% of NO conversion was observed over CoZSM-5 catalyst in the presence of propane at the same temperature range [8]. However, zeolite-based catalysts suffer from instability in hydrothermal conditions leading to catalysts deactivation [14]. Therefore, other catalytic systems such as zirconium oxide-based catalysts have been attracted more attention for HC-SCR due to

high acidity, hydrothermal stability and water tolerance [15,16]. Nonetheless, their low surface area and weak interaction with active components [5,6] keep them far from being a proper catalyst for industrial applications. Hence, many researches have been devoted to overcome these disadvantages and improve catalytic performance. For instance, a combination of zirconium with a mesoporous silica results in increased catalyst surface area, enhanced interaction with active components and formation of some Lewis and Brönsted acid sites which is desirable for a catalyst [17–21].

Two distinct methods, i.e. direct and post synthesis methods, can be used to synthesize Zrincorporated SBA-15 [22]. In the direct synthesis method (D), Zr is introduced to the SBA-15 structure during the hydrothermal synthesis of SBA-15 [23], while in the post synthesis method (P), incorporation of the metal is carried out through the chemical grafting on the synthesized SBA-15 as a second step [24]. Although high amounts of Zr is favored to achieve increased acidity and to enhance the interaction between the support and the active components, both techniques have limitations in Zr loading content, while retaining the intact structure of the SBA-15. High Zr loading brings about structural collapsing in the case of the former and pore blockage and surface area reduction in the case of the latter.

The objective of this paper is to develop a high Zr-loaded SBA-15 support material by using a combination of direct and post synthesis methods (DP). The application of the cobalt-doped support, synthesized by this innovative approach, was evaluated in NOx reduction under lean conditions and compared with those prepared by the conventional methods.

### 2 Experimental

### 2.1 Support and Catalyst preparation

*Zr-SBA-15 synthesis by direct synthesis method (D):* The established method reported by Gracia et al. [25] with some modification was applied for Zr-SBA-15 preparation by direct synthesis method. Amphiphilic triblock copolymer P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) as the structure directing agent was dissolved in hydrochloric acid solution at 35°C to produce a clear micelle solution. Then, appropriate amount of zirconium precursor (ZrONO<sub>3.xH2</sub>O) was added to the solution prior to tetraethyl orthosilicate addition. The mixture was kept under stirring at 35°C for 24 h. The resulting gel with a molar composition of 0.0171 P123: 1 Si: 0.05-0.2 Zr: 0.3 HCI: 206.35 H<sub>2</sub>O was then transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 100°C for 24 h under autogenous pressure. The final product, ZrSBADx (x represents the mole ratio of Si/Zr), was filtrated, washed several times with deionized water, dried at 60°C overnight and calcined at 600°C for 8 h with a heating rate of 1°C. min<sup>-1</sup>.

*Zr-SBA-15 synthesis by post synthesis method (P):* The method reported by Gutiérrez et al. [24] was applied with some modification for the preparation of the post-synthesized Zr-SBA-15. SBA-15 was prepared according to the method described elsewhere [26]. Then, appropriate amount of SBA-15, zirconium precursor (Zirconium (IV) propoxide [Zr(n-PrO)4] (70 wt % solution in 1-propanol)) and absolute ethanol, as solvent for chemical grafting, with a molar composition of 1 Si: 0.22 - 0.88 Zr: 13.7 solvent, were mixed overnight at room temperature under nitrogen gas. Excess Zr(n-PrO)<sub>4</sub> was eliminated by filtering and washed with three sequential aliquots of absolute ethanol. The obtained material, ZrSBAPx (x represents the mole ratio of Si/Zr), was then dried overnight at room temperature under nitrogen gas, and finally calcined at 550°C for 6 h with a heating rate 1°C. min<sup>-1</sup>.

*Zr-SBA-15 synthesis by combined direct-post synthesis method (DP):* ZrSBAD10 was first prepared using the above-explained procedure with Si/Zr of 10. Then, appropriate amount of prepared ZrSBAD10, zirconium precursor and absolute ethanol with a weight composition of 1 ZrSBAD10: 1.74-6.96 Zr(n-PrO)4:10.5 absolute ethanol, were mixed overnight under nitrogen gas. The slurry was filtered and washed with three sequential aliquots of absolute ethanol to eliminate excess Zr(n-PrO)4. The obtained material, ZrSBADPx (x represents the weight ratio of Si/Zr), was dried overnight at room temperature under nitrogen gas prior to calcination at 550°C for 6 h with a heating rate 1°C. min<sup>-1</sup>.

*Catalyst preparation:* ZrSBAD10, ZrSBAP2 and ZrSBADP2 and SBA-15 were used as support for Co-based catalyst preparation via the incipient wetness impregnation technique [27]. A required volume of aqueous solution of cobalt acetate tetrahydrate (Co (CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O) was impregnated into the support to obtain a desired content of Co on the support structure (1, 2, 4 and 10 wt %). The impregnated supports were dried overnight at 70°C and calcined at 550°C for 5 h in the open air with a heating rate of 1°C. min<sup>-1</sup>. These catalysts were denoted by the support preparation method and the cobalt content. For instance, Co4/ZrSBADP2 indicates that the support was prepared by DP technique with a weight ratio of Si/Zr equal to 2 and the catalyst contains 4wt% cobalt (Table 1). Moreover, a 2%Ag/Al<sub>2</sub>O<sub>3</sub> catalyst as a benchmark was prepared with the same impregnation and heat treatment procedures. A requisite volume of an aqueous solution containing the required amount of AgNO<sub>3</sub> was added dropwise onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

#### 2.2 Characterization

Prepared supports and catalysts were characterized by means of various methods including Powder X-ray diffraction technique (XRD), nitrogen adsorption and desorption, X-ray

photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF), Fourier transform infrared spectroscopy (FTIR).

PANalytical X-ray diffractometer (model X'pert Pro) and powder X-ray diffraction system (model PW1830 (Philips), 2KW, Cu anode, graphite monochromator) were used to determine the crystallinity of the materials. The scanning range ( $2\theta$ ) was adjusted in the range of 0.3-3° and 10-90° for low and high angle spectra, respectively.

N<sub>2</sub> adsorption-desorption were conducted by a Coulter SA3100 surface area analyzer at liquid nitrogen temperature. The samples were outgassed at 250°C for 120 min prior to the analysis. The specific surface areas of the supports and catalysts were determined in the linear region of the Brunauer–Emmett–Teller (BET) equation (relative pressure between 0.05 and 0.22). The total pore volume was calculated at relative pressure of 0.98.

XPS experiment was carried out by a Kratos Axis Ultra DLD multi-technique XPS instrument under ultra-high vacuum to analyze the surface chemistry of the materials. A monochromatic Al K $\alpha$  X-ray source (excitation energy, h $\nu$  = 1486.6 eV) at a voltage of 10 kV and a current of 15 mA was used as the energy source. The low and high resolution spectra were acquired at 70 and 20 eV pass energy, respectively. C(1s) at a binding energy of 284.6 eV was used as reference for the spectra correction.

Elemental composition of the prepared supports and catalysts was determined by XRF using a JEOL JSX-3201Z XRF. The X-ray source for the experiments was obtained when the voltage and current of the tube was adjusted at 30 kV and 0-1 mA, respectively.

FTIR was used to identify the functional moieties of prepared supports. Infrared spectrum of samples was collected by KBr pellet technique in the wave number range of 4000-400  $cm^{-1}$  at room temperature with a FTS 6000 FTIR spectrometer.

The surface acidity was measured by a pulse chromatographic technique approaching conditions of gas-chromatography linearity. The experiment was carried out in gas-phase at 300°C. The adsorption of pyridine (PY) and 2,6-dimethylpyridine (DMPY) as probe molecules (basic compounds) in a dynamic mode was conducted to measure the total acidity (sum of Brönsted and Lewis acid sites) and Brönsted acid sites, respectively [28]. Typically, a very small amount of probes molecules were injected into a modified gas chromatograph through a microreactor containing 50 mg of samples. The probe molecules were adsorbed by the sample until the saturation level from where the peaks of the compounds were detected by GC. Subsequently, the amounts of adsorbed PY and DMPY were measured.

### 2.3 Catalytic activity tests

The HC-SCR reaction was carried out in a fixed bed stainless steel reactor and fed with a continuous feed gas consisted of nitric oxide (500ppm), propane (500-2000ppm), oxygen (3-10 vol%), water vapor (0-7 vol%) and helium as balance. The gas flow rate was regulated at  $100\text{ml}.\text{min}^{-1}$  (GHSV equal to  $12000\text{h}^{-1}$ ). Typically, 0.5 g of catalyst powder was loaded between two glass wool layers into the reactor. The loaded reactor was placed in a Carbolite tube furnace in order to provide the desired temperature (controlled by an additional thermometer) for the reaction. Effluent gases were analyzed by a gas chromatograph (HP 6890 series) equipped with Porapak Q, Hayesep D columns and a TCD detector to determine the concentration of N<sub>2</sub>, CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> at steady state condition. The effects of various parameters including reaction temperature, catalyst composition and reactant concentration were evaluated. N<sub>2</sub> yield was considered as the NOx reduction performance of the catalyst and was calculated as follows:

NO conversion to 
$$N_2(\%) = \frac{[N_2]_{\text{produced}}}{[NO]_{\text{in}}}$$
 (Eq1)

where  $[N_2]_{out}$  and  $[NO]_{in}$  represent the moles of  $N_2$  in the outlet and NO in the feed stream, respectively.

### **3** Results and discussion

Production of a support with 2-D hexagonal structure as well as homogeneous dispersion and deposition of Zr was aimed in the preparation of a high Zr-loaded SBA-15. These two characteristics are essential for the material to be used as support for catalyst preparation applicable in HC-SCR reaction.

### 3.1 Catalysts and supports characterization

#### 3.1.1 Elemental analysis

In order to find out the effect of synthesis method on Zr content of the prepared materials, the metal contents (Si and Zr) of the prepared supports was measured and tabulated in Table 1. The elemental analysis results indicate that the Zr content in the direct synthesized supports (ZrSBADx) is inversely proportional to Si/Zr ratio in the initial synthesis gel. Although the highest Zr loading is achieved at a Si/Zr ratio of 5 (ZrSBAD5), the hexagonal structure of SBA-15 was completely distorted according to the XRD pattern (section 3.1.2). Therefore, the highest content of Zr (5.1 wt%) was obtained when Si/Zr was regulated at 10 while the well-ordered mesoporous structure of the SBA-15 remained intact. These results are in good agreement with literature [5].

The loading of Zr in the post synthesized support (ZrSBAPx) was considerably increased compared to the ZrSBADx while retaining the intact structure of the SBA-15. In ZrSBAP2, 16.7 wt % of Zr loading was achieved when Si/Zr ratio was adjusted to a value of 2.24, where the 2-

D hexagonal structure of SBA-15 was almost remained intact. It was also observed that the SBA-15 structure could accommodate the heteroatoms up to a saturation level and decreasing the Si/Zr ratio from 4.54 to 1.13 did not result in any increase in the Zr content. The highest amount of loaded Zr into the SBA-15 structure in this work (16.7 wt%) is lower than that obtained by Gutiérrez et al. (23.4 wt%) [29] which might be due to difference in solvent used (dry ethanol, 99.999%). A part of the alkoxide (zirconium precursor) can take part in hydrolysis as a side reaction in the presence of the water content of the absolute ethanol solvent leading to the formation of zirconium hydroxide precipitate [30]. However, from the practical point of view, using dry ethanol in industry scale is not applicable due to its high cost.

According to Table 1, the introduction of higher amounts of Zr into the SBA-15 structure has been facilitated by using the DP technique. Zr content in the SBA-15 structure significantly increased and reached 32.1 wt% (ZrSBADP2) which is 6 and 2 times higher than those of the direct (ZrSBAD10) and post synthesized (ZrSBAP2) supports, respectively. Moreover, the hexagonal structures of the prepared supports remained unchanged compared with that of the pure SBA-15 with no considerable collapses (Section 3.1.2). The considerably high Zr loading can be attributed to an enhanced interaction between the acid sites on the ZrSBAD10 and zirconium precursor (Zr(n-PrO)<sub>4</sub>) used in the post-synthesis method. In addition, according to Degirmenci et al.[31], the concentration of the silanol groups, (SiO)<sub>3</sub>Si — OH, is significantly increased upon direct synthesis of support. This high content of silanol groups might lead to an enhanced interaction between the zirconium precursor and the support through chemical grafting, subsequently resulting in more Zr contribution in the ZrSBADPx structure through either substitution in the framework or deposition on the surface.

### 3.1.2 X-ray diffraction pattern

The low and high angle diffraction patterns of the SBA-15, supports and catalyst, depicted in Figure 1a - b demonstrate that the intensity of the diffraction peaks related to DP-synthesized material with the highest Zr content slightly decreased, however well-ordered mesoporous crystal structure of the SBA-15 almost remained intact. This can be ascribed to the structural stability of the supports and catalyst at high calcination temperature essential for NOx reduction catalysts [32,33]. In addition, although a high Zr-loaded material (as high as 30 wt%) could be synthesized through the direct method using a Si/Zr ratio of 5 (ZrSBAD5), the well-ordered mesoporous structure was completely distorted, as testified by the XRD pattern. High-angel X-ray diffraction pattern of the Zr-loaded materials (Figure 1b) did not exhibit diffraction peaks at  $2\theta = 30^{\circ}$ ,  $35^{\circ}$ ,  $50^{\circ}$ , and  $60^{\circ}$  related to the tetragonal ZrO<sub>2</sub> crystalline phase on the supports [34]. This indicates that despite the significantly high Zr loading made by the DP method, Zr was dispersed homogeneously throughout the SBA-15 structure without any agglomeration.

### **3.1.3** Textural properties

The textural properties of the developed supports, SBA-15 as a reference and the prepared catalysts with various content of the cobalt are tabulated in Table 2. The surface area and pore volume are inversely proportional to the contribution of Zr into the SBA-15 framework. SBA-15 with no Zr content showed the highest specific surface area (905 m<sup>2</sup>. g<sup>-1</sup>) and total pore volume (1.2 cm<sup>3</sup>. g<sup>-1</sup>), while these two parameters decrease to 548 m<sup>2</sup>. g<sup>-1</sup> and 0.7 cm<sup>3</sup>. g<sup>-1</sup> for ZrSBADP2 with the highest Zr loading. A slight 2-D hexagonal structural modification as a result of Zr incorporation accounts for a reduction in the surface area and pore volume [5,24,25], which is confirmed by XRD results as well (Figure 1). A slight decrease in BET surface area and pore volume was observed after cobalt loading. The decreasing trend was directly proportional to

the cobalt content. A 29% reduction of the surface area was observed when the cobalt content increased from 1 wt% to 10 wt%. This trend demonstrates that the structural modification was more pronounced in the presence of a higher content of the cobalt species. Despite this reduction, the surface area of the catalysts was still higher than those of the zeolites and noble metal-based catalysts [15,35,36]. The large surface area of the prepared catalysts, resulting in more active sites for the chemisorption of the reactants and thus higher reaction rate, can be considered as one of the main advantages of the DP synthesis technique [37].

Nitrogen adsorption/desorption isotherms, shown in Figure S1, imply that all the samples exhibited the typical type IV isotherm with H1-type hysteresis loop characteristic of the mesoporous materials with a highly uniform size distribution according to the IUPAC classification [38].

#### 3.1.4 XPS analysis

The chemical state of Si, Zr and O atoms of the prepared supports was investigated by XPS. The XPS spectra of the Si- $2p_{3/2}$  (Figure 2) revealed that two distinct peaks for all the prepared supports were distinguished at a binding energy (BE) of approximately 103 and 105 eV. By comparing the spectra of the supports and SBA-15, a new Si environment was observed after the modification of SBA-15 with Zr irrespective to preparation method. A peak with a binding energy centered at about 104.5 eV emerged after the SBA-15 modification which is characteristic of the Si - O - Zr, while the bond at a BE of 103.6 eV is ascribed to Si - O - Si [39]. This suggests that Zr atoms were successfully introduced into the SBA-15 framework by all the techniques used.

XPS spectra of O1s (Figure 3a-c) show three distinct peaks associated with Si — O (at ca. 533 eV), Si — O — Zr (at ca. 532.5 eV) and Zr— O (at ca. 531 eV) for the various supports. In

addition, an obvious difference can be detected between the intensity of Zr-O in different supports. The intensity of Zr — O is directly proportional to the Zr content of the supports and in the order of ZrSBADP2 > ZrSBAP2 > ZrSBAD10. In addition, no peak at 528-529 eV related to Zr - O of pure  $ZrO_2$  was observed during XPS experiment [5,25,40]. As shown in Figure 4, no crystalline phase of ZrO2 was distinguished in the XPS spectra of Zr3d for different Zr-modified SBA-15. The Zr 3d<sub>5/2</sub> spectra of ZrSBADP2, ZrSBAP2 and ZrSBAD10 centered at 183, 183.2 and 183.4 eV, respectively, are far from 182.1 eV related to  $Zr^{4+}$  in  $ZrO_2$  cluster [41]. The deconvoluted XPS spectra of the catalysts are shown in Figure 5a-d and Table 3. For Co1/ZrSBADP2 and Co2/ ZrSBADP2, the core level binding energies of Co2p<sub>3/2</sub> were centered at 782.3 and 782.4 eV, respectively. Two satellites corresponding to two spin-orbital peaks also emerged at 787 eV and 786.8 eV, respectively. These BE values associated with satellite shakeup features indicate that the oxidation state of Co in these two catalysts is 2+ [42]. In addition, the core level BE values of  $Co2p_{1/2}$  for both samples was determined at 798.1 eV which is close to that of  $Co^{2+}$  ions. Also, the satellite for  $Co2p_{1/2}$  was observed at 803.9 and 803.7 eV for Co1/ZrSBADP2 and Co2/ZrSBADP2, respectively. These results further suggest that the majority of the cobalt atoms are present as Co<sup>2+</sup> clusters in tetrahedral coordination in Co1/ZrSBADP2 and Co2/ZrSBADP2 catalysts [43,44]. Co4/ZrSBADP2 showed two BE values for each of Co2p<sub>3/2</sub> and Co2p<sub>1/2</sub> at 782 and 783.7 eV, and 797.2 and 798.5 eV, respectively. In addition, two satellite related to the two spin-orbital peaks were observed 787.1 and 803.8 eV, respectively. These results further verify that cobalt atoms are present in oxidation state of (II) in Co4/ZrSBADP2. The existence of the second peak for Co2p<sub>3/2</sub> (centered at 783.7 eV) and Co2p<sub>1/2</sub> (centered at 798.5 eV) implies that some of the cobalt (II) species exist in octahedral coordination and/or cobalt oxide in Co4/ZrSBADP2 [45]. Similar trend can be observed for

Co10/ZrSBADP2. However, the intensities of the second peaks of  $Co2p_{3/2}$  and  $Co2p_{1/2}$  were higher than those of Co4/ZrSBADP2 (Table 3).

### 3.1.5 FTIR analysis

The incorporation of Zr into the SBA-15 framework was studied by FTIR spectroscopy (Figure S2). All the samples exhibited a band around 3440 cm<sup>-1</sup> and at 1634 cm<sup>-1</sup> assigned to O — H stretching vibration mode of the silanols groups bonded with the hydrogen and Zr — OH stretching vibration, respectively[46]. The intensity of the broad vibrational bands centered at 3440 cm<sup>-1</sup> and 1634 cm<sup>-1</sup> are directly proportional to the concentration of the hydroxyl and adsorbed water molecules which are affected by Zr content [47]. ZrSBADP2 with highest Zr content exhibited the highest intensity of O — H vibrational bands.

A broad strong band between 1200 and 810 cm<sup>-1</sup> was observed for all the samples. This band is comprised of several bands; the bands at 1200 cm<sup>-1</sup> and 1080 cm<sup>-1</sup> are related to asymmetric stretching vibration of SiO<sub>4</sub> units, the band at around 970 cm<sup>-1</sup> is assigned to Si— O— Zr symmetric stretching, the band at 880 cm<sup>-1</sup> is assigned to Si— O<sup> $\delta$ </sup> (non-bridging oxygen atoms), and the band at 803 cm<sup>-1</sup> is ascribed to symmetric stretching of Si— O [46,48]. The presence of the band at 970 cm<sup>-1</sup> in spectrum of Zr-loaded SBA-15 (related to Si— O — Zr) suggests that Zr is effectively introduced into the SBA-15 framework [16]. Since no IR band in the range of 910 and 970 cm<sup>-1</sup> was observed for the SBA-15, the presence of the band at 970 cm<sup>-1</sup> for the Zr-modified supports can be considered as an obvious evidence for the isomorphous contribution of Zr ions [49]. Furthermore, the intensity of the band at 970 cm<sup>-1</sup> is directly proportional to the Zr loading where the largest intensity of the band was observed for ZrSBADP2. This phenomenon might be related to greater substitution and deposition of Zr species either in the framework or on the surface of the SBA-15 structure during the DP modification process.

The broad adsorption band between 600 cm<sup>-1</sup> and 400 cm<sup>-1</sup> centered at 460 cm<sup>-1</sup>, is assigned to Zr — O— Si and/or Si — O— Si vibration [16,46,50]. Since, the same band was observed for SBA-15 as well, the contribution of Si — O — Si band cannot be excluded.

FTIR analysis of catalyst with highest cobalt content (Co10/ZrSBADP2) was performed for comparison with the support (ZrSBADP2). The result showed that the spectrum pattern of the catalyst was comparable to the support with negligible difference (Figure S2).

### 3.1.6 Surface acidity analysis

As given in Table 2, the supports and catalysts exhibited both Brönsted and Lewis acid sites. The quantities and simultaneous presence of these two types of acid sites play a critical role in HC-SCR reactions [1]. It has been demonstrated that the quantities of the Brönsted and Lewis acid sites are affected by the material preparation method. The Brönsted and Lewis acid sites of the ZrSBAD10, ZrSBAP2 and ZrSBADP2 were measured to be 92 and 29µmol. g<sup>-1</sup>, 96 and 32  $\mu$ mol. g<sup>-1</sup>, and 99 and 37  $\mu$ mol. g<sup>-1</sup>, respectively. This trend is in line with the trend of Zr content in the supports, where ZrSBAD10 with the lowest content of Zr exhibited the lowest acidity, and ZrSBADP2 with the highest Zr content showed the highest acidity. The relationship between the Zr content and acidity is in good agreement with literature where a direct proportional relationship between acidity and Zr content of mesoporous silica were reported [5,51,52]. The acidity of the catalysts did not change significantly after Co loading into the support. Lewis and Brönsted acidity decreased slightly from 37 to 34  $\mu$ mol. g<sup>-1</sup> and from 97 to 91 µmol. g<sup>-1</sup>, respectively, when Co content increases from 1wt% to 10 wt%. Since the concentration and strength of Brönsted and Lewis acid sites play an important role in NOx reduction with hydrocarbons [35,53–55], ZrSBADP2-supported cobalt catalysts possess a high potential to be applied as active catalysts in C<sub>3</sub>H<sub>8</sub>-SCR reaction.

### **3.2** Catalytic performance

#### 3.2.1 Effect of cobalt content

NO conversion to N<sub>2</sub> (%) over the catalysts with various cobalt contents at a temperature range of 250-500°C is shown in Figure 6. Three distinct temperature ranges was considered, namely 250-300°C, 350-400°C and T  $\geq$  450°C. At 300°C, the catalysts with higher content of cobalt, Co10/ZrSBADP2 and Co4/ZrSBADP2, exhibited 25 % and 21 % N<sub>2</sub> yield, respectively, which were higher than those of Co2/ZrSBADP2 (18 %) and Co1/ZrSBADP2 (5%). At 400°C, the catalyst with 2 wt% cobalt exhibited 70 % N2 yield which was 50% and 20% higher than those of Co10/ZrSBADP2 and Co4/ZrSBADP2. Also, the cobalt content of 1 wt% was proved to be sufficient to show higher NO conversion (67 %) compared to the Co10/ZrSBADP2 and Co4/ZrSBADP2 at the same temperature. In the high temperature region, the activity of the catalysts were inversely proportional to the cobalt content. Co1/ZrSBADP2 showed 45 % N2 yield at 500°C while Co10/ZrSBADP2 had only 12 % N2 yield. Therefore, it is demonstrated that the activity of the catalysts was strongly affected by the cobalt content. Since ZrSBADP2 exhibited neither NO reduction through the entire temperature range, nor CO<sub>2</sub> formation at  $T \leq 350$  °C, it is concluded that cobalt species play a crucial role in reduction of NO through propane activation that results in the formation of intermediate components, namely, oxygenated hydrocarbons (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>). In addition, no N<sub>2</sub>O formation was detected as the by-product of the reaction during the NO reduction over the catalysts at different temperatures. In order to elucidate the effect of cobalt content on the catalyst performance, two general competitive reactions were considered in the SCR of NO with propane:

$$2NO + C_3H_8 + 4O_2 \rightarrow N_2 + 4H_2O + 3CO_2$$
(R1)

$$\mathbf{C_3H_8} + \mathbf{50_2} \rightarrow \mathbf{4H_2O} + \mathbf{3CO_2} \tag{R 2}$$

It should be noted that reactions (R1) and (R2) are not intended as a SCR mechanism over the catalysts. In addition, the oxidation of NO to NO<sub>2</sub> might also occur during the NO reduction in the presence of the oxygen [44].

The proceeding of reactions (R1) and (R2) is strongly affected by the nature of the cobalt species on the catalysts, which is, in turn, influenced by the amount of cobalt content [13,56,57]. High concentration of cobalt in Co10/ZrSBADP2 results in the formation of cobalt species which has weak interactions with the support and can be easily reduced at low temperature. Moreover, the production of cobalt oxides as a form of nano-sized Co<sub>3</sub>O<sub>4</sub>, active in NO reduction at low temperature, might occur in the high-loaded cobalt catalyst which was already validated by XPS analysis and has been reported by Martinez et al. [58]. The oxidation of NO to NO<sub>2</sub>, as one the main steps in HC-SCR, is improved in the presence of these cobalt oxide species which in turn facilitate the activation of hydrocarbons for NOx reduction at low temperatures. However, at high temperatures, reaction (R2) is favored to a greater extent by Co<sub>3</sub>O<sub>4</sub> than reaction (R1) [59] which leads to a significant deactivation of Co10/ZrSBADP2.

Co4/ZrSBADP2 was less active than Co10/ZrSBADP2 at low temperature however it showed a better activity at high temperature. This behavior might be due to the presence of various cobalt species on the catalyst. A mixture of Co<sup>2+</sup> ions and cobalt oxide is present on the two catalysts. However, from the XPS results (Table 3), the intensity of the cobalt oxide species in Co10/ ZrSBADP2 was much higher than Co4/ZrSBADP2. Thus, Co4/ZrSBADP2 was less active than Co10/ZrSBADP2 at low temperatures whereas it showed a better activity at higher temperature. Furthermore, it is well known that the formation of NOx-ad species over the catalyst is one the main important steps in HC-SCR reaction [60,61]. The types of the formed NOx-ad species are affected by the metal loading. Highly stable nitrate species including

monodentate and bidentate nitrates can be produced over the high metal-loaded catalysts [62]. Considering that the dissociation of these stable species occurs at high temperatures, direct oxidation of propane (R2) is also accelerated at such high temperatures by high-loaded metal catalyst. Thus, the overall NO reduction decreases over Co10/ZrSBADP2 and Co4/ZrSBADP2 at high temperatures.

The cobalt oxide species (active at  $T \le 300$  °C) are not present in the catalyst with low cobalt content. Therefore, Co2/ZrSBADP2 possesses merely Co<sup>2+</sup> ions in tetrahedral coordination and cobalt silicate which favors the reaction (R1) at T > 300 °C. Moreover, further decrease in the cobalt content, from 2 wt% to 1 wt%, did not lead to any significant change in the catalytic activity of Co2/ZrSBADP2 and Co1/ZrSBADP2 at  $T \ge 400$  °C. However, a slight change in the performance at T < 400 °C can be assigned to the difference in the dispersion of the cobalt species on the support and/or interaction with the support. The intensity of the shake-up satellite related to Co2p<sub>3/2</sub> and 2p<sub>1/2</sub> of the Co2/ZrSBADP2 were higher than that of Co1/ZrSBADP2 (Table 3). This phenomenon indicates that the interaction of the cobalt species in Co1/ZrSBADP2 with the support is stronger than that of Co2/ZrSBADP2 [43] which results in a slight decrease in the reducibility of the cobalt species at low temperatures [58] and therefore, lower activity of the Co1/ZrSBADP2 at T < 400 °C.

Since Co2/ZrSBADP2 exhibited better NO reduction compared to the other catalysts, a 2 wt % cobalt loading was considered as an optimum loading ratio for further study.

### **3.2.2** Effect of Zr content

In order to evaluate the effect of Zr content on the catalyst performance, the supports, ZrSBAD10, ZrSBAP2,ZrSBADP2, and SBA-15 were loaded with 2 wt % cobalt and their NOx conversion efficiency was determined. As depicted in Figure 7, the catalyst performance was

directly proportional to the Zr content. Co2/ZrSBADP2 with the highest Zr concentration exhibited the highest N<sub>2</sub> yield at all temperatures, while Co2/SBA and Co2/ZrSBAD10 did not show any considerable N<sub>2</sub> yield. This phenomenon can be attributed to the difference in the acidity of the supports by the Zr content, where the amount of Lewis and Brönsted acidity is ZrSBADP2 > ZrSBAP2 > ZrSBAD10. The conversion of NO to N<sub>2</sub> occurs via the formation of nitrates adsorbed (NOx-ad) species through several sequential reactions on the Lewis acid sites [35]. Subsequently, the NOx-ad species are reduced to N<sub>2</sub> by the oxygenated hydrocarbons (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>) [60,61]. Thus, it can be inferred that an increase in the Lewis acid density (increase in the Zr content) will elevate the amount of the NOx ad-species, which, in turn, will increase the overall conversion of NO to N<sub>2</sub>. Moreover, it has been reported that HC-SCR is also promoted by Brönsted acidity of the catalysts [63–67]. Orlyk [64] showed that the catalytic efficiency of the oxide systems is directly proportional to the concentration of Brönsted acid sites of the catalysts surface. This can be explained by the fact that the formation of oxygenated hydrocarbons (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>), as intermediate components in HC-SCR, and hydrocarbon activation are promoted by Brönsted acid centers [63,67]. Through the novel DP technique, higher contents of Lewis and Brönsted acid sites can be achieved which can highly enhance the NO to N<sub>2</sub> conversion.

### **3.2.3** Effect of propane concentration

The performance of the optimum catalyst was evaluated at two concentrations of propane (500 and 1250 ppm) while other parameters were maintained constant (500 ppm of NO, 6 vol % of O2 in helium as balance with the total flow rate of 100 ml. min<sup>-1</sup>). According to Figure 8a, different trends at two temperature regimes ( $T \le 350^{\circ}$ C and  $T \ge 400^{\circ}$ C) were observed during NO reduction. At  $T \le 350^{\circ}$ C, increasing the propane concentration from 500 ppm to 1250 ppm did not lead to any enhancement in the NO to N<sub>2</sub> conversion. This result is in line with the amount of

C<sub>3</sub>H<sub>8</sub> conversion to CO<sub>2</sub> at T  $\leq$  350 °C (Table 4). C<sub>3</sub>H<sub>8</sub> conversion to CO<sub>2</sub> was about 2 % and 15% at 300 and 350°C, respectively, with respect to that at 500°C in the presence of 1250 ppm of propane. Nonetheless, the conversion increased to 7% and 37% in the presence of 500 ppm of propane at the same temperatures. This phenomenon might be explained by the fact that in the presence of high concentration of propane, some of the active centers of the catalyst are blocked by the higher fraction of unreacted hydrocarbon species, because the temperature is not high enough to proceed the reaction towards N<sub>2</sub> and CO<sub>2</sub> formation in order to recover the active centers.

At 400, 450 and 500°C, N<sub>2</sub> yield increased significantly from 70% to 100 %, 60% to 98% and 36% to 68%, respectively, with increasing the propane concentration. At high temperatures, higher concentration of reducing agent increases the formation of oxygenated hydrocarbon intermediate species ( $C_xH_yO_z$ ) which results in a strong enhancement in the catalytic activity towards N<sub>2</sub> formation [36,68,69]. Moreover, at higher reducing agent concentration, the metal sites on the catalyst are reduced more efficiently which results in higher NOx reduction [36].

#### 3.2.4 Effect of oxygen concentration

The efficiency of Co2/ZrSBADP2 was evaluated under various concentrations of oxygen (Figure 8b). In the presence of 3 vol % of oxygen, a 23 % and 65 % N<sub>2</sub> yield was achieved at 350 and 400°C, respectively. By increasing the oxygen concentration from 3 vol % to 6 vol %, NO conversion to N<sub>2</sub> was favored at  $T \le 400$ °C and reached 54% and 70% at 350°C and 400°C, respectively. These results are consistent with the previous studies in which the oxidation of NO to NO<sub>2</sub> has been shown as one of the main steps in HC-SCR reaction in the presence of oxygen [70,71]. In addition, the formation of partial oxidized hydrocarbon species (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>) proceeds via the interaction with oxygen atoms and/or nitrogen containing intermediate species which leads to

the reduction of nitrogen oxide species to N<sub>2</sub>. This phenomenon can be more pronounced in the presence of oxygen, [71–73]. On the other hand, the activity of the catalyst was slightly suppressed when the concentration of O<sub>2</sub> increased from 6 vol % to 10 vol % over the entire temperature range. The maximum NO conversion to  $N_2$  decreased to 60% in the presence of 10 vol % of oxygen at 400°C. This observation is in accordance with the results reported by Lou et al. [74] and Kotsifa et al. [75]. They have attributed this reduction to the increase in the oxidation rate of C<sub>3</sub>H<sub>8</sub> to CO<sub>2</sub> (R 2) at higher oxygen concentration [76], as validated in Table 4. It was shown that the increase in oxygen concentration from 6 vol % to 10 vol % resulted in 13 %, 21 % and 16 % increase in the quantity of CO<sub>2</sub> formation at 300, 350 and 400°C, respectively. Moreover, it is well-recognized that the ratio of hydrocarbon to oxygen surface coverages  $(\theta_{HC}/\theta_0)$  plays an important role in HC-SCR reaction rate [77]. In the presence of high concentration of propane and the absence of oxygen, hydrocarbonaceous species are deposited on the catalyst active sites which diminish the NO reduction. Nonetheless, deposited hydrocarbonaceous species are removed with the adsorbed oxygen (O-ad) as a result of the introduction of O<sub>2</sub> in the feed gas. Hence, the active sites are recovered and become available for further NO reduction. However, excessive increase in oxygen concentration leads to active site poisoning with O-ad due to insufficient amount of propane to recover the active sites [75,77]. It is interesting to note that the catalyst could restore its activity when the oxygen concentration was returned to 6 vol % of the inlet concentration. These results confirm the high tolerance of Co2/ZrSBADP2 under severe condition, such as car exhaust [14].

#### 3.2.5 Effect of water vapor

Figure 8c shows the performance of the catalyst in the presence of 7 vol% water vapor, as a typical value for a lean-burn engine exhaust [36]. The activity of the catalyst was remarkably

enhanced by the presence of water vapor in the range of 300-350°C, where the N<sub>2</sub> yield increased from 18 % to 34 % and from 54 % to 70 % at 300 and 350°C, respectively. This can be explained by the fact that, in the absence of water vapor, the active surface sites of catalysts might be covered by the carbonaceous species resulting in the suppression of the catalyst performance. Presence of water vapor has a depression effect on the accumulation of carbonaceous species on the catalyst surface, and thus leads to an increase in the catalytic activity [78]. This rationale can be validated by comparing the CO<sub>2</sub> formation in the presence and absence of the water vapor (Table 4) as well as propane conversion (Figure 8c). In the presence of water vapor, the propane conversion was higher than that in the dry feeding at all examined temperatures. The results indicate that the presence of water vapor causes a significant increase in the formation of CO<sub>2</sub> in the range of 300-350°C. The formation of CO<sub>2</sub> in the presence of water vapor was about 2 and 2.5 times more than those in the absence of the steam at 300 and 350°C, respectively. These findings are in good agreement with previous reports [7,79]. Furthermore, the formation of organic nitroso or nitro species (R — NO, R — NO<sub>2</sub>) via gas phase or surface reaction has been evidenced as intermediate species in HC-SCR system [7,80,81]. Nitroso or nitro species are adsorbed as NCO and CN species through several reaction steps. Ultimately, NCO and CN species can be converted to  $N_2$ ,  $CO_2$  and  $H_2O$  through the following reaction pathways; (i) oxidation by NO<sub>2</sub> gas in which the reaction rate might increase in the presence of water vapor, (ii) conversion to ammonia through hydrolysis by water vapor and then selective reduction of NO by the formed NH<sub>3</sub> [7,82]. Thus, the presence of water vapor enhances the NO reduction to N<sub>2</sub> irrespective to the reaction pathways.

Figure 8c also shows that the activity of the catalyst was not affected by the water vapor at temperatures higher than 400°C. The extent of CO<sub>2</sub> formation was not affected by the steam

at  $T \ge 400$  °C (Table 4) which is accordance with the previous report [78]. This indicates that the presence of water vapor did not change the reaction pathway or the availability of the propane for NO reduction at high temperatures [83]. Furthermore, the competition between water adspecies and reactants/intermediate species for the active sites are weakened at high temperatures, because the abundance of water ad-species is considerably decreased and therefore the NO reduction will be independent of the water vapor presence [15].

In contrast to the most developed catalysts which are deactivated by H<sub>2</sub>O [82,84,85], the high tolerance of Co<sub>2</sub>/ZrSBADP2 towards H<sub>2</sub>O renders it suitable for practical NOx reduction applications in lean burn HC-SCR.

#### 3.2.6 Long-term activity

The long-term stability of the prepared catalyst in the real exhaust condition is a crucial concern for practical applications. The activity of Co2/ZrSBADP2 was evaluated for longer reaction time (60 h) at 400°C in the presence and absence of water vapor (Figure 9).No significant decrease in N<sub>2</sub> yield was observed during the prolonged reaction. The catalyst could retain a 70 % NO conversion to N<sub>2</sub> for 60 h regardless of the presence or absence of water vapor. This indicates the hydrothermal stability of the catalyst structure and the cobalt active components on the support under reaction conditions.

The efficiency of the developed catalyst was more pronounced when it was compared with 2%Ag/Al<sub>2</sub>O<sub>3</sub> as a benchmark catalyst. 2%Ag/Al<sub>2</sub>O<sub>3</sub> did not show any NOx reduction at  $T \leq 350$ °C. Moreover, NO conversion to N<sub>2</sub> of 8%, 20% and 28% was achieved at 400, 450 and 500°C, respectively (Figure 6). These results are in a good agreement with the literature in which Ag/Al<sub>2</sub>O<sub>3</sub> has been used as a catalyst in HC-SCR [14,68,86,87]. Shimizu et al.[86]reported that 10% of NO was converted to N<sub>2</sub> by 2%Ag/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of 6000 ppm of

propane at 400°C. Similar result was observed by Hernández-Terán et al. [87]. This implies that Co/ZrSBADP2 is more active than the benchmark catalyst, which is beneficial for the practical application in NOx reduction and depletion of unburned HC emission (Figure S3).

### 4 Conclusion

Highly loaded Zr-SBA-15 mesoporous materials were prepared by a novel DP technique. Zr content of the prepared material (32.1 wt%) was considerably higher than those prepared through the conventional methods. Characterization of the catalysts and supports showed an ordered mesoporous structure with high specific surface area ( $548m^2$ . g<sup>-1</sup>), homogeneous dispersion of Zr and high acidity. A cobalt-based catalyst was prepared by loading various amounts of the cobalt into the developed support. A 70 % N<sub>2</sub> yield was achieved over the catalyst with a cobalt content of 2 wt% in the absence of water vapor at 400°C. Presence of water vapor not only did not suppress the NOx conversion efficiency, but also significantly increased the N<sub>2</sub> yield at relatively low temperatures. The evaluation of the long-term stability of the catalyst at high temperatures showed that the catalyst was able to retain its high efficiency for a prolonged period of 60 h without any deactivation.

The promising activity of Co2/ZrSBADP2 under various extreme conditions, i.e. long-term stability and presence of water vapor, confirms the potential applicability of the catalyst for NOx conversion in real lean-burn gas and natural-fueled engines. Meanwhile, it is cost effective since no noble metal was used.

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Figure 1. Low (a) and high-angle (b) XRD pattern of the supports and catalyst



Figure 2. XPS Si2p spectra of (a) SBA-15, (b) ZrSBAD10, (c) ZrSBAP2, (d) ZrSBADP2



Figure 3. XPS O1s spectra of (a) ZrSBAD10, (b) ZrSBAP2, (c) ZrSBADP2



Figure 4. XPS Zr3d spectra of the supports



**Figure 5.** XPS Co2p spectra of (a) Co1/ZrSBADP2, (b) Co2/ZrSBADP2, (c) Co4/ZrSBADP2, (d) Co10/ZrSBADP2



Figure 6. Effect of cobalt content on NO conversion to N<sub>2</sub> (%). Reaction conditions: [NO] = 500 ppm,  $[O_2] = 6 \text{ vol } \%$ ,  $[C_3H_8] = 500 \text{ ppm}$  in He, flow rate = 100 ml. min<sup>-1</sup>



Figure 7. Effect of Zr content on NO conversion to N<sub>2</sub> (%). Reaction conditions:[NO] = 500 ppm,  $[O_2] = 6 \text{ vol } \%$ ,  $[C_3H_8] = 500 \text{ ppm}$  in He, flow rate = 100 mi. min<sup>-1</sup>



**Figure 8.** Effect of propane (a) oxygen (b) and water vapor concentration (c) on NO conversion to N<sub>2</sub> (solid line) and propane conversion (dash line) over Co2/ZrSBADP2. Reaction conditions:  $[NO] = 500 \text{ ppm}, [O_2] = 6 \text{ vol } \%, [C_3H_8] = 500\text{-}1250 \text{ ppm}, H_2O= 0\text{-}7 \text{ vol}\%$  in He, flow rate = 100 ml. min<sup>-1</sup>



**Figure 8.** Effect of propane (a) oxygen (b) and water vapor concentration (c) on NO conversion to N<sub>2</sub> (solid line) and propane conversion (dash line) over Co2/ZrSBADP2. Reaction conditions:  $[NO] = 500 \text{ ppm}, [O_2] = 6 \text{ vol } \%, [C_3H_8] = 500\text{-}1250 \text{ ppm}, H_2O= 0\text{-}7 \text{ vol}\%$  in He, flow rate = 100 ml. min<sup>-1</sup>



**Figure 8.** Effect of propane (a) oxygen (b) and water vapor concentration (c) on NO conversion to N<sub>2</sub> (solid line) and propane conversion (dash line) over Co2/ZrSBADP2. Reaction conditions:  $[NO] = 500 \text{ ppm}, [O_2] = 6 \text{ vol } \%, [C_3H_8] = 500\text{-}1250 \text{ ppm}, H_2O= 0\text{-}7 \text{ vol}\%$  in He, flow rate = 100 ml. min<sup>-1</sup>



Figure 9. Effect of long-term stability condition on Co2/ZrSBADP2. Reaction conditions: [NO] = 500 ppm, [O<sub>2</sub>] = 6 vol %, [C<sub>3</sub>H<sub>8</sub>] = 500 ppm, H<sub>2</sub>O = 0-7 vol % in He, T= 400 °C, flow rate = 100 ml. min<sup>-1</sup>

Sample	(Si/Zr) <sup>1</sup>	$Zr (wt\%)^2$	Si (wt%)	Co ( wt%)
ZrSBAD20	20	2.1	97.9	-
ZrSBAD10	10	5.1	94.9	-
ZrSBAD5	5	30.5	69.5	-
ZrSBAP4	4.54	16.5	83.5	-
ZrSBAP2	2.27	16.7	83.3	-
ZrSBAP1.5	1.51	14.7	85.3	-
ZrSBAP1	1.13	14.5	85.5	-
ZrSBADP4	4.14	19	81	-
ZrSBADP2	2.07	32.1	67.9	-
ZrSBADP1.5	1.38	24.8	75.2	-
ZrSBADP1	1.03	25.2	74.8	-
Co1/ZrSBADP2	2.07	31.8	67.4	0.8
Co2/ZrSBADP2	2.07	31.5	66.7	1.8
Co4/ZrSBADP2	2.07	30.7	65.2	4.1
Co10/ZrSBADP2	2.07	25.7	64.5	9.8

**Table 1.** Elemental analysis of the supports and catalysts by XRF

Si/Zr mole ratio in initial synthesis gel
 Zr, Si and Co content in the final materials measured by XRF

Commis	$\mathbf{S}(\mathbf{z},\mathbf{z}^2,\mathbf{z})$	$V_{\rm eff}$ (see 3 (s)	Total acidity	Brönsted acidity	Lewis acidity	
Sample	S(m²/g)	vp (cm <sup>3</sup> /g)	(µmol PY/g)	(µmol DMPY/g)	(µmol/g)	
SBA-15	905	1.2	$NM^1$	NM	NM	
ZrSBAD10	787	1.1	128	96	32	
ZrSBAP2	570	0.88	121	92	29	
ZrSBADP2	548	0.7	136	99	37	
Co1/ZrSBADP2	510	0.7	134	97	37	
Co2/ZrSBADP2	467	0.68	133	96	37	
Co4/ZrSBADP2	433	0.65	129	94	35	
Co10/ZrSBADP2	363	0.55	125	91	34	
1- Not measured						

**Table 2.** Physical and chemical properties of the supports and catalysts

	Co2p <sub>3/2</sub>			Shake-up Co2p <sub>3/2</sub>		Co2p <sub>1/2</sub>				Shake-up Co2p <sub>1/2</sub>		
Samples	Binding energy (eV)	Intensity (area)	Binding energy (eV)	Intensity (area)	Binding energy (eV)	Intensity (area)	Binding energy (eV)	Intensity (area)	Binding energy (eV)	Intensity (area)	Binding energy (eV)	Intensity (area)
Co10/ZrSBADP2	781.8	4249	783.2	6534	787.3	9494	797.8	2944	799.3	2033	804.1	4406
Co4/ZrSBADP2	782	6073	783.7	1265	787.1	4769	797.2	475.3	798.5	1509	803.8	2124
Co2/ZrSBADP2	782.4	2364	_	_	786.8	3085	_	_	798.1	1310	803.7	1226
Co1/ZrSBADP2	782.3	1059		—	787	1384	_		798.1	707	803.9	613

### Table 3. Deconvoluted XPS Co2p spectra of the catalysts

Temperature (°C)									
	250	300	350	400	450	500			
$\left(\frac{[\mathrm{CO}_2]_{atT}}{[\mathrm{CO}_2]_{\mathrm{at500°C}}}\right)^a$	0.03	0.07	0.37	0.8	1	1			
$\left(\frac{[\mathrm{CO}_2]_{atT}}{[\mathrm{CO}_2]_{at500^{\circ}\mathrm{C}}}\right)^{b}$	0.02	0.02	0.15	0.56	0.89	1			
$\frac{[\mathbf{CO}_2]^c}{[\mathbf{CO}_2]^d}$	1	1.13	1.21	1.16	1.04	1.02			
$\frac{[\mathrm{CO}_2]^e}{[\mathrm{CO}_2]^f}$	1	1.99	2.55	0.95(1.1) <sup>g</sup>	1(1)	1(1)			

Table 4. The ratio of CO<sub>2</sub> formation in the different reaction conditions

a- [C<sub>3</sub>H<sub>8</sub>] = 500 ppm b- [C<sub>3</sub>H<sub>8</sub>] = 1250 ppm c= [CO<sub>2</sub>] in the presence of 10 vol % of O<sub>2</sub>

 $d= [CO_2] \text{ in the presence of 6 vol % of O_2}$  $d= [CO_2] \text{ in the presence of 6 vol % of O_2}$  $e= [CO_2] \text{ in the presence of 7 vol % of H_2O}$  $f- [CO_2] \text{ in the presence of 0.0 vol % of H_2O}$ 

 $g - \frac{[CO_2]_{7 \ vol \ \% \ of \ vapor}}{[CO_2]_{0.0 \ vol \ \% \ of \ vapor}}, \text{ without NO in the feed stream}$