



# Influence of co-fed gases ( $O_2$ , $CO_2$ , $CH_4$ , and $H_2O$ ) on the $N_2O$ decomposition over (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts

Nayara F. Biturini<sup>1</sup> · Ana Paula N. M. Santos<sup>1</sup> · Marcelo S. Batista<sup>1</sup>

Received: 1 October 2018 / Accepted: 16 November 2018 / Published online: 22 November 2018  
© The Author(s) 2018

## Abstract

The influence of co-fed gases ( $O_2$ ,  $CO_2$ ,  $CH_4$ , and  $H_2O$ ) on the  $N_2O$  decomposition over (Co or Fe)-BETA and (Co, Fe)-ZSM-5 catalysts prepared by ion exchange method was investigated.  $Co^{2+}$  ions and oxo dinuclear Co species were identified in Co-ZSM-5 and Co-BETA catalysts. Isolated and oligomeric  $Fe^{3+}$  species in cationic sites and  $Fe_2O_3$  particles were found on surface of the Fe-ZSM-5 and Fe-BETA catalysts. Cobalt catalysts were more actives than iron catalysts for the direct decomposition of  $N_2O$ . Conversion of  $N_2O$  over Fe-BETA and Fe-ZSM-5 was remained stable when co-fed  $O_2$ ,  $CO_2$ , and  $CH_4$ , but decreases with water vapor. However, Co-BETA and Co-ZSM-5 showed much larger reaction rate for  $N_2O$  decomposition and were very stable when co-fed  $O_2$ ,  $CO_2$ ,  $CH_4$ , and especially  $H_2O$ . The results showed that the higher  $CH_4$  consumption during  $N_2O$  reaction over Co-BETA and Co-ZSM-5 was due to  $CH_4$  combustion.

**Keywords**  $N_2O$  decomposition · Co-fed gases · Iron species · Cobalt species · ZSM-5 zeolite · BETA zeolite

## Introduction

Nitrous oxide ( $N_2O$ ) is a potent greenhouse-effect gas with global warming potential (GWP) per molecule of about 300 times and 21 times higher than that of carbon dioxide ( $CO_2$ ) and methane ( $CH_4$ ), respectively. Nitrous oxide is not only a greenhouse gas, but also contributes to stratospheric ozone depletion [1–3]. The increase in anthropogenic  $N_2O$  emissions (combustion, production of nitric and adipic acids, etc.) shows that the development of effective methods to reduce these emissions is therefore urgent. Consequently, extensive efforts are focused on catalysts for the decomposition of  $N_2O$

✉ Marcelo S. Batista  
marcelobatista@ufsj.edu.br

<sup>1</sup> Chemical Engineering Department, Federal University of São João Del Rei, Campus Alto Paraopeba, Rodovia MG 443, Km 5, POBox 131, Ouro Branco, MG CEP 36420-000, Brazil

into harmless  $N_2$  and  $O_2$  due to their efficiency, simplicity and low preparation costs [4, 5].

$N_2O$  decomposition has been evaluated on several catalysts, such as supported noble metals [6–8], transition metal oxides [8–12], and metal exchanged zeolites [13–15]. Noble metal based catalysts as Pt and Rh are active at low temperatures. However, the higher cost of these catalysts and the conversion reduction when co-fed with  $O_2$  and/or  $H_2O$  make their industrial application unviable [16]. Additionally, metal oxide based catalysts have been proposed for high temperature operation conditions. However, Liu et al. [8] as well as Yu et al. [17] showed that the  $N_2O$  conversion decreases in presence of  $H_2O$ ,  $CO_2$ , and  $O_2$ , which are commonly found in industrial exhausts. Recent progress in the  $N_2O$  decomposition reaction has been studied with the focus on transition-metal (Cu, Fe, Co)-modified zeolite catalysts [13–15, 18, 19]. Efforts dedicated to Cu-ZSM-5 have shown that decomposition of  $N_2O$  is inhibited by  $O_2$  or  $H_2O$  co-fed [18]. On the other hand, Fe-zeolite catalysts have been outstanding due to their high activity and resistance in co-fed of  $CH_4$ ,  $CO$ ,  $O_2$  and  $SO_2$  [20, 21]. Fe-ZSM-5 has been most studied experimentally and theoretically for the decomposition of  $N_2O$  [22, 23]. It is believed that isolated  $Fe^{3+}$  and oligonuclear  $Fe_x^{3+}O_y$  clusters on the exchanged sites affects the catalytic performance [13, 22]. Furthermore, it is also notable that Co-sites were more active than Fe-sites due to lower activation energy barrier for the direct decomposition of  $N_2O$  [19, 24]. According to some authors [13, 20], the activity of (Fe, Co)-zeolite catalysts also depends on the intrinsic properties of each zeolitic structure.

Some studies with BETA zeolite have shown attractive and advantageous characteristics of this material for catalysis, such as: wide pore opening, three-dimensional channel system, large specific area, high thermal and hydrothermal stability and shape selectivity [13, 14]. In terms of the zeolite topology, Fe-BETA was the most effective material between various commercial zeolites (MFI, FER, MOR, FAU) with similar Si/Al ratios for the decomposition of  $N_2O$  [25] exhibiting superior activity in comparison with Fe-ZSM-5 [26]. Additionally, Liu et al. [19] reported that the activity of Co-BETA was higher than that of Fe- or Cu-BETA comparing by the turnover frequency (TOF).

Although some studies for  $N_2O$  decomposition by using beta-type zeolites has been done as previously reported [19, 25, 26], these works were not done with co-fed gases commonly found in industrial emissions. In addition, the performance of cobalt-containing zeolites for  $N_2O$  decomposition is so far not well established. Therefore, the objective of this work was to study the influence of co-fed  $O_2$ ,  $CO_2$ ,  $H_2O$  and  $CH_4$  on the direct decomposition of  $N_2O$  over (Co, Fe)-BETA and (Co, Fe)-ZSM-5 catalysts. These catalysts were prepared by ion exchange method and its characterization using XRD,  $H_2$ -TPR and UV–VIS spectroscopy was also discussed.

## Materials and methods

### Catalyst preparation

The (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts were prepared by ion-exchange methods using commercial Na-ZSM-5 (ALSI-PENTA Zeolithe GmbH)

and  $\text{NH}_4$ -BETA (TRICAT) zeolites with similar Si/Al molar ratios. The parent zeolite (3 g) was added to 1 mol/L aqueous solutions (150 mL) of iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) at 50 °C. The mixture was vigorously stirred for 12 h. The sample was exchanged three times under the same conditions. Between each ion-exchange, the mixture was filtered; the solid was washed with distilled water and dried at 110 °C. Finally, the (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts were obtained after further calcination in muffle oven at 650 °C for 2 h under static air.

### Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD), temperature programmed reduction with  $\text{H}_2$  ( $\text{H}_2$ -TPR) and UV–Visible Diffuse Reflectance Spectroscopy (UV–VIS). XRD analyzes were performed by the powder method using a Rigaku diffractometer (Miniflex 600) with Cu tube, Ni-filtered, operating at 40 kV, 15 mA and Cu  $K_\alpha$  radiation. The speed of the goniometer used was 2° ( $2\theta$ )/min, the angle ranging between 5 and 80° ( $2\theta$ ). The crystal phases were determined by correlating the diffraction patterns with those in the X'Pert HighScore reference.

$\text{H}_2$ -TPR analyses were performed on SAMP3 apparatus (Termolab Equipment, Brazil) equipped with a thermal conductivity detector (TCD). A trap was used to remove the water stemming from the reduction before the gas of the reactor outlet was sent to the TCD. TPR started with a ramp of 10 °C/min from 100 °C until 1000 °C. A flow of 30 mL/min from a high purity mixture of 2 V %  $\text{H}_2$  in Ar was used.

UV–VIS analyses were carried out in an Ocean Optics USB2000 spectrometer using a quartz cell. Before the measurement, the samples were dried at 120 °C for 2 h to remove the water molecule or OH groups. Samples were scanned in the range of 200–800 nm. The reflectance data were converted to the Schuster–Kubella–Munk function,  $F(R) = (1 - R)^2/2R$ , where R is the diffuse reflectance obtained directly from the spectrometer.

### Catalytic activity

Catalytic tests for  $\text{N}_2\text{O}$  decomposition over (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts were carried out in U-shaped quartz reactor with an inner diameter of 9 mm. An electric furnace equipped with PID temperature control was used to heat the reactor. About 40 mg of catalyst were placed on fixed bed of quartz-wool inside the reactor. For all the experiments, 60 mL/min from a mixture of 10 V %  $\text{N}_2\text{O}$  in He was flowed continuously into the reactor, corresponding to a GHSV of 30,000  $\text{h}^{-1}$ . Catalytic performance started with a ramp of 10 °C/min from 25 to 600 °C. The effect of co-fed gases on catalytic performance of catalysts was studied by adding 10 V %  $\text{O}_2$ , 10 V %  $\text{CO}_2$ , 10 V %  $\text{CH}_4$  and 10 V %  $\text{H}_2\text{O}$  vapor (by saturator) into the reaction mixture at 600 °C whereas the concentration of  $\text{N}_2\text{O}$  was still 10 V %, and the total flow of the gas was still 60 mL/min. The gaseous mixture flows were adjusted by electronic controllers (Brooks Instrument 0254).

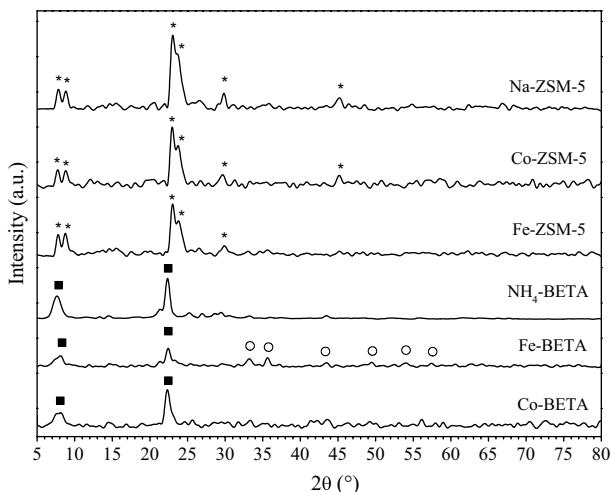
The reactor was coupled in line to mass spectrometer (Pfeiffer Vacuum, Thermo-Star GSD 320T) for gas analysis:  $N_2$  ( $m/z=28$ ),  $O_2$  ( $m/z=32$ ),  $N_2O$  ( $m/z=44$  and  $30$ ),  $CH_4$  ( $m/z=16$  and  $15$ ),  $CO_2$  ( $m/z=44$ ) and He ( $m/z=4$ ). The conversion of nitrous oxide was calculated through Eq. 1.

$$\text{Conversion of } N_2O (\%) = \left( \frac{N_2O_{(in)} - N_2O_{(out)}}{N_2O_{(in)}} \right) \times 100\% \quad (1)$$

where  $[N_2O]_{in}$  refers to molar flow of  $N_2O$  at room temperature, and  $[N_2O]_{out}$  refers to molar flow of  $N_2O$  at an elevated temperature. The reaction rate was calculated as mol of  $N_2O$  converted per hour/total mol of Fe or Co (measured by XRF), using conditions of kinetic regime, temperature established and catalytic activity stable [27, 28].

## Results and discussion

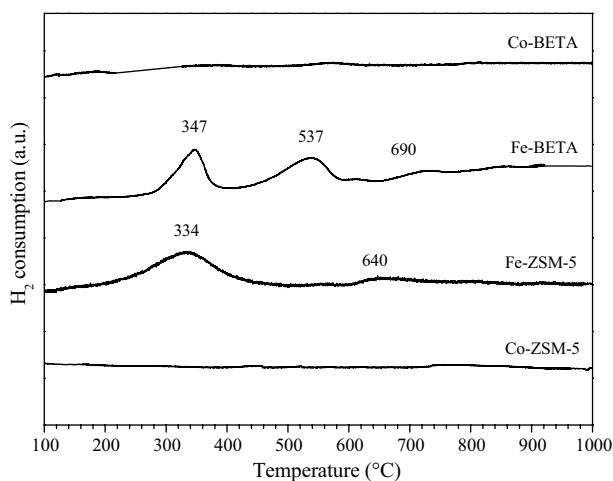
Fig. 1 shows the XRD patterns of the ZSM-5 and BETA zeolites and also of the (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts. The MFI and BEA crystalline structures were well preserved even after exchange with Fe or Co ions. (Co, Fe)-ZSM-5 catalysts showed characteristics peaks of precursor ZSM-5 zeolite in  $2\theta=7.8^\circ$ ,  $8.7^\circ$ ,  $15.7^\circ$ ,  $23.0^\circ$ ,  $23.7^\circ$ ,  $29.7^\circ$ ,  $45.1^\circ$  (PDF 37-0359). In its turn, (Co, Fe)-BETA catalyst showed characteristics peaks of BETA-typed zeolite in  $2\theta=7.6^\circ$ ,  $22.3^\circ$  (PDF 48-0074). Close examination of Fig. 1 shows slight reductions in the peak intensities of the Fe-ZSM-5 and Fe-BETA catalysts due to the higher X-ray absorption coefficient of Fe compounds [29, 30]. No diffraction



**Fig. 1** XRD patterns of ZSM-5 and BETA zeolites and (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts. Typical peaks of: (asterisk) ZSM-5, (filled square) BETA and (open circle)  $Fe_2O_3$

peaks from  $\text{FeO}_x$  nanoparticles were observed for Fe-ZSM-5 evidencing only the presence of Fe-exchanged active species in the zeolite structure. However, the existence of tiny  $\text{FeO}_x$  species cannot be totally excluded as considering their amounts are possibly below the XRD detection limit. On the other hand, Fe-BETA shows characteristic peaks of  $\text{Fe}_2\text{O}_3$  in  $2\theta = 33.2^\circ, 35.6^\circ, 40.9^\circ, 49.5^\circ, 54.1^\circ, 62.5^\circ, 64.1^\circ$  (PDF 01-1053). The absence of  $\text{Co}_3\text{O}_4$  peaks in Co-ZSM-5 and Co-BETA diffractograms indicates the presence of Co-exchanged species in the zeolite structure. In view of the solubility, the precipitation of  $\text{Fe}(\text{OH})_3$  ( $K_{\text{SP}} = 2.7 \times 10^{-39}$ ,  $25^\circ\text{C}$ ) is more thermodynamically expected than  $\text{Co}(\text{OH})_2$  ( $K_{\text{SP}} = 5.9 \times 10^{-15}$ ,  $25^\circ\text{C}$ ) for our catalysts. However, the preparation conditions (low pH and temperature at  $50^\circ\text{C}$ ) used in this work appear to have prevented further formation of cobalt oxides.

Fig. 2 shows the TPR profiles of (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts. No reduction peaks were observed in profiles of Co-ZSM-5 and Co-BETA, confirming the absence of cobalt oxides on surface of these catalysts. These results are also consistent with the XRD measurement. Most Co species exist in the form of  $\text{Co}^{2+}$  at the ion exchange sites and the further reduction of  $\text{Co}^{2+}$  into  $\text{Co}^0$  occurred above  $1000^\circ\text{C}$  [31]. As seen from Fig. 2, the first two peaks (347 and  $537^\circ\text{C}$ ) of Fe-BETA and the peak at  $334^\circ\text{C}$  of Fe-ZSM-5 were mainly assigned to reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (in cations or oxo-cations) [32]. Fe-ZSM-5 and Fe-BETA catalysts showed a slight shoulder at  $640$  and  $690^\circ\text{C}$ , respectively, which were attributed to the reduction of  $\text{FeO}$  to  $\text{Fe}^0$  [19, 26], confirming that trace amount of  $\text{Fe}_2\text{O}_3$  aggregated on zeolite surface. It has been reported that, the corresponding  $\text{H}_2$  consumption of  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$  was actually comprised in the former two peaks of Fe-BETA and together with the first Fe-ZSM-5 peak [26]. Further reduction of  $\text{Fe}^{2+}$  into  $\text{Fe}^0$  was not observed under the conditions used, it usually occurred above  $1000^\circ\text{C}$  and causes the collapse of the zeolite structure [33]. In general, Co- and Fe-exchanged sites with the zeolite framework were



**Fig. 2**  $\text{H}_2$ -TPR profiles of (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts

predominant in the (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts. These cationic species are known as the most active sites for the direct decomposition of nitrous oxide.

The further information on the cobalt and iron species present in the (Co, Fe)-ZSM-5 and (Co, Fe)-BETA catalysts were studied by UV–VIS spectroscopy, as shown in Fig. 3. Co-BETA (Fig. 3a) and Co-ZSM-5 (Fig. 3b) showed a band located at 200–235 nm corresponding to transitions from the oxygen atoms to  $\text{Co}^{2+}$  ions in the cationic sites, and a band of the ligand to metal  $\text{O} \rightarrow \text{Co}^{2+}$  charge-transfer of the -oxo dinuclear Co species at 240–350 nm and broad absorption in the region of d–d transitions at 360–750 nm of the octahedral  $\text{Co}^{2+}$  ions in ion-exchange position, according to the literature reports [34–36]. Wichterlová et al. [37, 38] assigned the bands in the visible range to  $\text{Co}^{2+}$  located at three different sites in the ZSM-5 and BETA, i.e.,  $\alpha$ - (680 nm),  $\beta$ - (460, 570, 613, 645 nm) and  $\gamma$ -sites (497 and 540 nm). In addition, both cobalt-catalysts are light pink in color, typical of the presence of  $[\text{Co}(\text{II})(\text{H}_2\text{O})_6]^{2+}$  compensating the negative charge of the zeolite framework. These results are consistent with the XRD and TPR measurements of these catalysts.

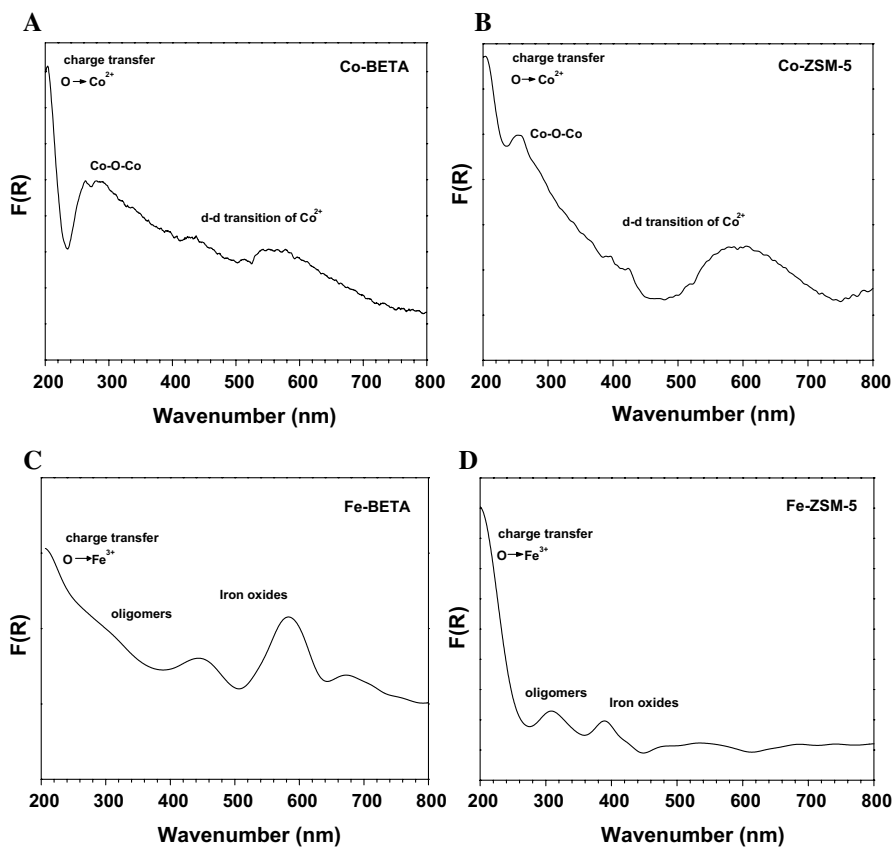
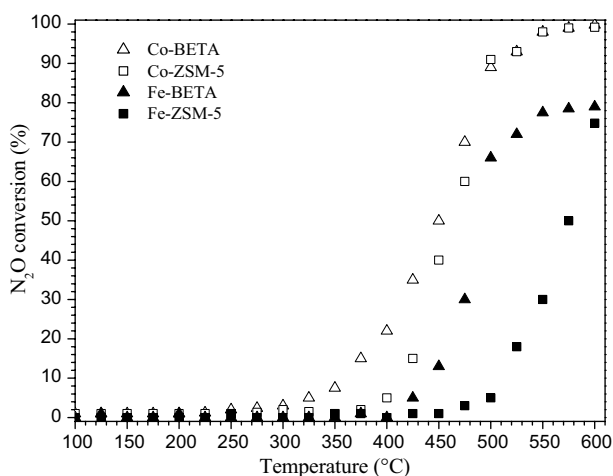


Fig. 3 UV–VIS spectra of: a Co-BETA, b Co-ZSM-5, c Fe-BETA and d Fe-ZSM-5

As for the UV–VIS spectra of Fe-BETA (Fig. 3c) and Fe-ZSM-5 (Fig. 3d), the two bands observed at 200–260 nm and at 260–360 nm corresponding to the typical ligand to metal charge transfer (LMCT) bands of isolated  $\text{Fe}^{3+}$  species in the cationic sites [19, 34] and isolated or oligomeric extraframework Fe species in zeolite channels [22], respectively. The bands at 360–460 nm (iron oxide clusters) and  $>450$  nm (large surface oxide species) can be associated to  $\text{Fe}_2\text{O}_3$  particles on zeolite surface [22]. Note that the spectrum of the Fe-ZSM-5 catalyst was characterized by a low intensity absorption edge at 550 nm reflecting low concentration of Fe oxide nanoparticles, which was not detected by XRD ( $<4$  nm), however observed by TPR. On the other hand, Fe-BETA showed a significant increase of the band above 500 nm confirming the present of large particles of  $\text{Fe}_2\text{O}_3$  on zeolite surface, as already commented by XDR and TPR.

Fig. 4 shows the  $\text{N}_2\text{O}$  conversions on (Co, Fe)-BETA and (Co, Fe)-ZSM-5 catalyst as a function of reaction temperature. It was found that the  $\text{N}_2\text{O}$  conversion rises very rapidly with the temperature on Co-ZSM-5 and Co-BETA, but much more smoothly on Fe-ZSM-5 and Fe-BETA. Co-species might be well dispersed as an ionic form, as verified by  $\text{H}_2$ -TPR, leading to increase of  $\text{N}_2\text{O}$  conversion. Therefore, cobalt-based catalysts were more actives than iron-based catalysts showing that cobalt species in ion-exchange position are more actives due to lower activation energy barrier for the direct decomposition of  $\text{N}_2\text{O}$ . Considering that the actual metal loads of Co-BETA (3.4%), Co-ZSM-5 (3.2%) Fe-BETA (6.5%) and Fe-ZSM-5 (0.3%) were different; the activities were compared by reaction rate. Results of the reaction rate calculation at 450 °C also showed that Co-BETA ( $14.2 \text{ h}^{-1}$ ) and Co-ZSM-5 ( $12.0 \text{ h}^{-1}$ ) were more effective catalysts than Fe-BETA ( $1.9 \text{ h}^{-1}$ ) and Fe-ZSM-5 ( $3.0 \text{ h}^{-1}$ ). In addition, the reaction rates of our cobalt-zeolite catalysts were much higher than those of cobalt oxides ( $\leq 1 \text{ h}^{-1}$ ) [39–41]. The reaction rates (called TOF) of Fe zeolite catalysts (BEA, FAU, MOR, FER) reported in the literature, are in the range  $0.03$ – $7.11 \text{ h}^{-1}$  at  $400$ – $500$  °C, depending critically on the preparation/

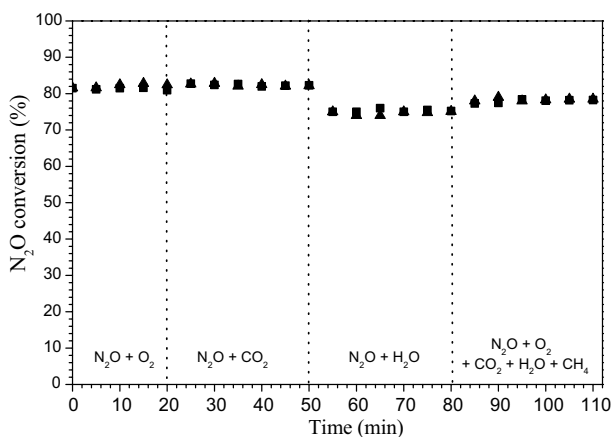


**Fig. 4**  $\text{N}_2\text{O}$  decomposition over (Co, Fe)-BETA and (Co, Fe)-ZSM-5 catalysts

pretreatment [23]. Therefore, the activity of our Fe-BETA and Fe-ZSM-5 catalysts is within the range of reaction rates found in the literature. As for the Co-catalysts, the reaction rate was comparable to those values reported in the literature [42, 43]. Reaction rate discrepancies of the previous and present works are mainly attributed to the different reaction conditions such as the  $m_{\text{cat}}$ , GHSV, and especially for the  $\text{N}_2\text{O}$  concentrations [19] and also the catalyst preparation [42].

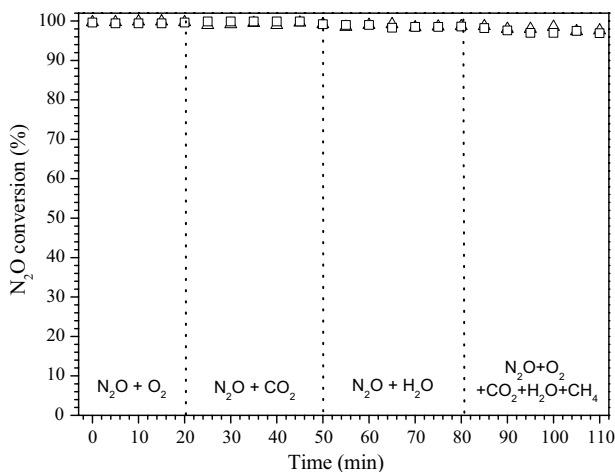
As noted, the nature of the host zeolite has a great influence on the reactivity of Fe and Co species with respect to  $\text{N}_2\text{O}$ . Co-BETA was the most active material at low temperatures. This can be understood to both the large amount of active sites and to the widely open porosity of the BEA structure. Co-BETA and Co-ZSM-5 catalysts show similar conversions at higher temperatures due to the mass transfer regime. However, it is known that the decomposition of  $\text{N}_2\text{O}$  over catalysts is inhibited mainly by  $\text{O}_2$  or  $\text{H}_2\text{O}$  co-fed. The inhibiting effect of  $\text{O}_2$  and  $\text{H}_2\text{O}$  vapor has been attributed to the competition adsorption between  $\text{N}_2\text{O}$  and  $\text{O}_2$  or  $\text{H}_2\text{O}$  [16, 19] and hydroxylation of the active sites by  $\text{H}_2\text{O}$  [23, 44].

Fig. 5 shows that the conversion of  $\text{N}_2\text{O}$  over Fe-BETA and Fe-ZSM-5 practically remained stable in the presence of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ , but decreases slightly ( $\sim 6\%$ ) was observed in the presence of water vapor. This deactivation in the presence of  $\text{H}_2\text{O}$  was associated with the hydroxylation of the active iron sites [23, 44]. The effect of periodic step changes of co-fed 10 vol% of  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$ , on the performance of over Co-BETA and Co-ZSM-5 at 600 °C are shown in Fig. 6. The  $\text{N}_2\text{O}$  conversion was about 99% without co-fed (no shown), consistent with the value seen in Fig. 4. Note that the  $\text{N}_2\text{O}$  conversion over Co-BETA and Co-ZSM-5 was maintained after the introduction of 10 V%  $\text{O}_2$  and 10 V%  $\text{CO}_2$ . In the presence of  $\text{H}_2\text{O}$ , no significant change was observed in the conversion of  $\text{N}_2\text{O}$  to both catalysts. These results indicated that cobalt sites were more resistant to hydroxylation than the iron sites exchanged in BETA and ZSM-5 zeolites. The  $\text{N}_2\text{O}$  conversion over



**Fig. 5** Effect of co-fed gases on the  $\text{N}_2\text{O}$  conversion over Fe-BETA (filled triangle) and Fe-ZSM-5 (filled square) catalysts. Condition: reaction at 600 °C and gas mixture: 10%  $\text{N}_2\text{O}$ , 10%  $\text{O}_2$ , 10%  $\text{CO}_2$ , 10%  $\text{CH}_4$ , 10%  $\text{H}_2\text{O}$  and inert balance

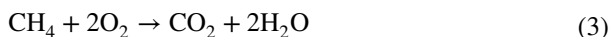
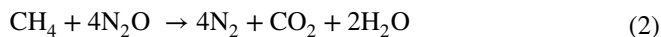




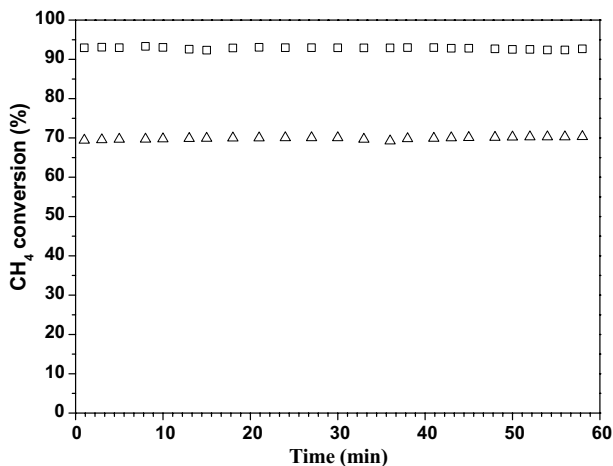
**Fig. 6** Effect of co-fed gases on the  $\text{N}_2\text{O}$  conversion over Co-BETA (open triangle) and Co-ZSM-5 (open square) catalysts. Condition: reaction at  $600^\circ\text{C}$  and gas mixture: 10%  $\text{N}_2\text{O}$ , 10%  $\text{O}_2$ , 10%  $\text{CO}_2$ , 10%  $\text{CH}_4$ , 10%  $\text{H}_2\text{O}$  and inert balance

Co-BETA and Co-ZSM-5 was also maintained after the introduction of all gases ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$ ). In general, Co-BETA and Co-ZSM-5 are highly active for the  $\text{N}_2\text{O}$  decomposition, showing reaction rate clearly much larger and, interestingly, are very stable in the presence of  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and especially  $\text{H}_2\text{O}$ , with a slight decay of conversion of  $0.06\%/h$ .

Methane is also a greenhouse gas that must be eliminated from the stream of effluent gases. For this purpose, the methane consumption was monitored during the  $\text{N}_2\text{O}$  reaction. Fig. 7 shows the  $\text{CH}_4$  conversion over Co-BETA and Co-ZSM-5 catalysts during  $\text{N}_2\text{O}$  reaction at  $600^\circ\text{C}$  co-fed with complete gas mixture ( $\text{N}_2\text{O} + \text{CH}_4 + \text{O}_2 + \text{CO}_2 + \text{H}_2\text{O}$ ). Note that  $\text{CH}_4$  consumption occurs on both cobalt-catalysts; however, Co-ZSM-5 consumes more  $\text{CH}_4$  than Co-BETA. It is known that the apparent activation energy for  $\text{N}_2\text{O}$  reduction by  $\text{CH}_4$  is very similar to that of direct  $\text{N}_2\text{O}$  decomposition ( $140\text{ kJ/mol}$ ) [20]. In the case of  $\text{N}_2\text{O}$  reduction by methane (Eq. 2), the stoichiometric amount requires to 1 mol of  $\text{CH}_4$  to reduce 4 mol of  $\text{N}_2\text{O}$ , i.e. maximum methane conversion of 25%. Thus, the higher methane consumption on Co-BETA (70%) and Co-ZSM-5 (92%) must be associated with the occurrence of  $\text{CH}_4$  combustion reaction (Eq. 3).



Our observations suggest that the reactions of  $\text{N}_2\text{O}$  decomposition and reduction of  $\text{N}_2\text{O}$  by  $\text{CH}_4$  proceed via different reaction mechanism and might occur over cobalt sites of the zeolite. Nobukawa et al. [45] measured the oxidation rates of methane with  $\text{N}_2\text{O}$  and  $\text{O}_2$ , and found that the intermediates of methoxy were oxidized with  $\text{N}_2\text{O}$  more rapidly than  $\text{O}_2$ . However, our results showed that the co-fed



**Fig. 7** CH<sub>4</sub> conversion over Co-BETA (open triangle) and Co-ZSM-5 (open square) during N<sub>2</sub>O reaction at 600 °C co-fed with complete gas mixture (N<sub>2</sub>O + CH<sub>4</sub> + O<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>O)

with complete gas mixture (N<sub>2</sub>O + CH<sub>4</sub> + O<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>O) did not change the N<sub>2</sub>O conversion over Co-BETA and Co-ZSM-5 catalysts.

## Conclusions

(Co, Fe)-BETA and (Co, Fe)-ZSM-5 catalysts prepared by ion-exchange method have Co<sup>2+</sup> ions, and oxo dinuclear Co species or isolated and oligomeric Fe<sup>3+</sup> species compensating the negative charge of the zeolite framework, as shown by UV–VIS spectroscopy. In addition, Fe<sub>2</sub>O<sub>3</sub> particles were found on surface of the Fe-ZSM-5 and Fe-BETA catalysts. Cobalt-catalysts were more actives than iron-catalysts for the direct decomposition of N<sub>2</sub>O. Conversion of N<sub>2</sub>O over Fe-BETA and Fe-ZSM-5 practically remained stable in the presence of O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>, but decreases slightly in the presence of water vapor. On the other hand, Co-BETA and Co-ZSM-5 were highly actives for the N<sub>2</sub>O decomposition, showing reaction rate clearly much larger and, interestingly, were very stable in the presence of O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and especially H<sub>2</sub>O, with a slight decay of conversion of 0.06%/h. The higher CH<sub>4</sub> consumption during N<sub>2</sub>O reaction on Co-BETA (70%) and Co-ZSM-5 (92%) was due to CH<sub>4</sub> combustion.

**Acknowledgements** The authors would like to acknowledge FAPEMIG (TEC-APQ-03361-15) for financial support of this research and Nayara Fernandes Biturini is grateful to the CAPES (Brazil) for a scholarship.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

1. Zhang X, Guan Y, Zhang S, Yang M, Zhao Y, Hao Z (2014) *J Mol Catal A* 395:202–209
2. IPCC (2013) *Climate Change 2013: the physical science basis. Contribution of working group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*
3. Frutos OD, Quijano G, Aizpuru A, Muñoz R (2018) *Biotechnol Adv* 36:1025–1037
4. Wu M, Wang H, Zhong L, Zhang X, Hao Z, Shen Q, Wei W, Qian G, Sun Y (2016) *Chin J Catal* 37:898–907
5. Melián-Cabrera I, Espinosa S, Mentruit C, Murray B, Falco L, Socci J, Kapteijn F, Moulijn JA (2018) *Ind Eng Chem Res* 57(3):939–945
6. Pares-Esclapez S, Illán-Gómez MJ, Lecea CS, Bueno-López A (2010) *Appl Catal B* 96:370
7. Pachatouridou E, Papista E, Iliopoulou EF, Delimitis A, Goula G, Yentekakis IV, Marnellos GE, Konsolakis M (2015) *J Environ Chem Eng* 3:815
8. Liu Z, He F, Ma L, Peng S (2016) *Catal Surv Asia* 20(3):121–132
9. Pietrogiamici D, Campa MC, Carbone LR, Tuti S, Occhiuzzi M (2016) *Appl Catal B* 187:218–227
10. Wang J, Feng M, Zhang HJ, Xu XF (2014) *J Fuel Chem Technol* 42:1464–1469
11. Zhou H, Huang Z, Sun C, Qin F, Xiong D, Shen W, Xu H (2012) *Appl Catal B* 125:492
12. Zabilskiy M, Djinović P, Tchernychova E, Tkachenko OP, Kustov LM, Pintar A (2015) *ACS Catal* 5:5357
13. Wang J, Xia H, Ju X, Fan F, Feng Z, Li C (2013) *Chin J Catal* 34:876–888
14. Sklenak S, Andrikopoulos PC, Boekf B, Jansang B, Nováková J, Benco L, Bucko T, Hafner J, Dědeček J, Sobalík Z (2010) *J Catal* 272:262–274
15. Moura APN, Batista MS (2017) *Matéria*. <https://doi.org/10.1590/s1517-707620170003.0190>
16. Lin Y, Meng T, Ma Z (2015) *J Ind Eng Chem* 28:138
17. Yu H, Tursun M, Wang X, Wu X (2016) *Appl Catal B* 185:110–118
18. Meng T, Ren N, Ma Z (2015) *J Mol Catal A* 404:233–239
19. Liu N, Zhang R, Chen B, Li Y, Li Y (2012) *J Catal* 294:99–112
20. Debbagh MN, Lecea CSM, Pérez-Ramírez J (2007) *Appl Catal B* 70:335–341
21. Pérez RJ, Kapteijn F, Mul G, Moulijn JA (2002) *Appl Catal B* 35(3):227–234
22. Richards N, Nowicka E, Carter JH, Morgan DJ, Dummer NF, Golunski S, Hutchings GJ (2018) *Top Catal*. <https://doi.org/10.1007/s11244-018-1024-0>
23. Xie P, Luo P, Ma Z, Huang C, Miao C, Yue Y, Hua W, Gao Z (2015) *J Catal* 330:311–322
24. Ryder JA, Chakraborty AK, Bell AT (2002) *J Phys Chem B* 106(28):7059–7064
25. Øygarden AH, Pérez-Ramírez J (2006) *Appl Catal B* 65(1–2):163–167
26. Chen B, Liu N, Liu X, Zhang R, Li Y, Li Y, Sun X (2011) *Catal Today* 175(1):245–255
27. Lente G (2013) *ACS Catal* 3(3):381–382
28. Blligaard T, Bullock RM, Campbell CT, Chen JG, Gates BC, Gorte RJ, Jones CW, Jones WD, Kitchin JR, Scott SL (2016) *ACS Catal* 6(4):2590–2602
29. Jouini H, Mejri I, Martínez-Ortígosa J, Cerrillo JL, Mhamdi M, Palomares AE, Delahay G, Blasco T (2018) *Solid State Sci* 84:75–85
30. Qi G, Yang RT (2005) *Appl Catal A* 287(1):25–33
31. Jong SJ, Cheng S (1995) *Appl Catal A* 126(1):51–66
32. Guzmán-Vargas A, Delahay G, Coq B (2003) *Appl Catal B* 42(4):369–379
33. Feng XD, Hall WK (1997) *J Catal* 166:368–376
34. Szama P, Pilar R, Mokrzycki L, Vondrova A, Kaucky D, Plsek J, Sklenak S, Stastny P, Klein P (2016) *Appl Catal B* 15(189):65–74
35. Beznis NV, Weckhuysen BM, Bitter JH (2010) *Catal Lett* 136(1–2):52–56
36. Castilho S, Borrego A, Henriques C, Ribeiro MF, Fernandes A (2017) *Inorg Chim Acta* 455:568–574
37. Dědeček J, Čapek L, Kaucký D, Sobalík Z, Wichterlova B (2002) *J Catal* 211(1):198–207
38. Szama P, Tabor E, Klein P, Wichterlova B, Sklenak S, Mokrzycki L, Pashkova V, Ogura M, Dedecek J (2016) *J Catal* 333:102–114
39. Jirátoá K, Kovanda F, Balabánová J, Koloušek D, Klegová A, Pacultová K, Obalová L (2017) *Reac Kinet Mech Cat* 121(1):121–139
40. Ciura K, Grzybek G, Wójcik S, Indyka P, Kotarba A, Sojka Z (2017) *Reac Kinet Mech Cat* 121(2):645–655
41. Wang Y, Hu X, Zheng K, Zhang H, Zhao Y (2018) *Reac Kinet Mech Cat* 123(2):707–721
42. Zhang X, Shen Q, He C, Ma C, Cheng J, Liu Z, Hao Z (2012) *Catal Sci Technol* 2(6):1249–1258

43. Smeets PJ, Meng Q, Corthals S, Leeman H, Schoonheydt RA (2008) *Appl Catal B* 84(3–4):505–513
44. Rutkowska M, Piwowska Z, Micek E, Chmielarz L (2015) *Microporous Mesoporous Mater* 209:54–65
45. Nobukawa T, Yoshida M, Kameoka S, Ito SI, Tomishige K, Kunimori K (2004) *J Phys Chem B* 108(13):4071–4079