Redox effects in Cu, Co or Fe in oxides nanocrystals with high catalytic activity for the acetonitrile combustion

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Abstract

The cobalt, copper and iron oxides were investigated in selective catalytic combustion (SCC) of acetonitrile toward N_2 in gas phase. Catalysts were characterized by physical–chemical technics like XRD, H_2 -TPR, DRS UV–Vis, whose confirmed crystalline phases of CuO , Co_3O_4 and Fe_2O_3 . Thermodynamic stability of crystalline phase from metal oxides ruled important contributions in redox properties and become able to compare clearly the catalytic activity of the three catalyst. Relationship between H_2 -TPR analysis and catalytic results obtained showed great relevance to understand how metal oxide works on reaction, who were related to easy redox process involved. SCC studies were carried out with range of 100–600 °C and Co_3O_4 showed best activity (100% conversion at 570 °C) and high selectivities to N_2 and CO_2 starting in lower temperature. Byproducts from nitrogen-compounds were observed in low quantities for all catalysts.

Keywords Selective catalytic combustion (SCC) · Acetonitrile · CuO · Co_3O_4 · Fe_2O_3

1 Introduction

Redox process is widely used in chemical process like energy store devices (ion batteries) [1], thermochemical storage [2], chemical looping combustion (CLC) [3], in the presence of hydrogen peroxide [4], advanced oxidation process (AOP) [5–7] and oxidation reactions in general [8, 9].

Metal oxide materials that can oxidize organic matter, afford a reduced material that can be reoxidized to close the loop. Recent years have seen substantial advances in the formulation and manufacture of these oxygen carrier materials and their incorporation into chemical looping reactors for the production of various chemicals. Reducible metal oxides are in solid state compounds exhibiting variable valence or oxidation states of the metal, such as CeO_2 , VO_x , FeO_x , CoO_x , MnO_x and CuO_x . Charge transfer or redox reactions are essential steps for the catalytic reaction at elevated temperatures. Many spinel ferrites have been

studied as candidate in redox reaction, example, $MeFe_2O_4$ ($Me = Mn, Ni, Zn, Co$ and Cu) as oxygen carriers or potentially reactive supports for oxygen carriers in oxidation reaction [10]. In route of these metal oxides like copper, cobalt and iron they have shown large utilization in catalytic process due to provide low cost raw materials, easy to manufacture in lab and nontoxic in moderate conditions.

Cobalt oxide is versatile in various industrial sectors, up to now five cobalt oxides, CoO , CoO_2 , Co_2O_3 , $CoO(OH)$ and Co_3O_4 , have been reported [11]. The activity of different Co_3O_4 facets that interacts with other substances, such as O_2 , H_2O , CO and heavy metals, is discrepant due to different geometric and electronic structures [12].

Copper has various oxidation states, such as Cu_2O and CuO . It was reported that Cu_2O was found to be more active than CuO for CO oxidation [13]. There are several $Cu(II)$ complexes including dinuclear $Cu(II)$ compounds which have been used as catalyst for the activation of C_{sp^3} –H bond. Different hydrocarbons have been utilized

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as the substrates such as methane, cyclohexane, cyclopentane. Oxidation of cyclohexane is useful because its oxidized products, mainly cyclohexanol and cyclohexanone, are of great industrial importance [14].

The chemistry of iron is enriched by the number of accessible spin states; including high-, intermediate-, and low-spin iron complexes. The known oxidation states of iron range from Fe(0) to Fe(VI), all of which have been observed experimentally. The Fenton ($\text{H}_2\text{O}_2/\text{FeII}$) or Fenton like ($\text{H}_2\text{O}_2/\text{FeIII}$) reaction, are well known reactions, which are used mainly to generate reactive oxygen species ($\text{HO}\cdot$ and $\text{HOO}\cdot$) with H_2O as by-product and are used widely in the treatment of waste water [15]. Iron catalysts have been employed on the industrial oxidation process of methanol to formaldehyde [16], and Fischer–Tropsch synthesis ($n\text{CO} + \{2n(+1)\}\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n(+2)} + n\text{H}_2\text{O}$) have considered an attractive way to convert natural/shale gas, coal, biomass, and CO_2 into clean liquid fuels and high value-added chemicals via syngas ($\text{H}_2 + \text{CO}$) [17].

Many studies have been presented about catalysts and reactions focused in organic matter oxidation or oxidation process itself, although some reactions still in a lack to understand redox property in catalysts, for example the selective catalytic combustion of nitriles (SCC).

Acetonitrile (CH_3CN) is a volatile organic compound that has received attention in recent years due to its potential atmospheric pollution index. There are different sources of acetonitrile in the atmosphere, one of them is from biomass burning [18]. Significant amounts of acetonitrile are also found in the exhaust gases in industrial plants for the production of acrylonitrile, drawing attention to their removal because of their high potential risk to the environment. Acetonitrile can be easily decomposed into hydrocyanic acid (HCN) vapors, a compound that in small strokes is highly toxic to humans and wildlife, which could lead to a significant environmental impact [19].

A technique that can be used to treat acetonitrile emissions is conventional combustion, but significant quantities of undesirable by-products such as nitrogen oxides (NO_x) could be generated, which would result in secondary air pollution, in addition to high energy cost, because this combustion work at high temperatures (above 800°C). However, selective catalytic combustion (SCC) would be a more assertive alternative because, with the addition of catalysts, this type of combustion occurs at a lower working temperature and with a higher formation of the products of interest, such as N_2 and CO_2 gases, thus more appropriate method for the treatment of acetonitrile emissions [20].

Catalysts based on metals Pt, Pd and Rh show good activity in the selective catalytic combustion of acetonitrile and acrylonitrile (SCC- CH_3CN) at low temperature, but does not yet as selective as the desired products

(N_2 and CO_2), generating nitrogen oxides (NO_x) besides the high cost of these catalysts for having noble metals. However, a number of catalysts based on metals like Cu, Co and Fe supported in zeolites have been used in SCC- CH_3CN , among which Cu catalysts obtained better catalytic activities and better selectivity and yield to N_2 [21]. Redox studies in SCC reactions have been presented as the background of the main effect of catalytic activity. The metal oxide redox processes in catalysts have not been so explored, and some works related the metallic dispersion level over supports or itself support effect in [21]. The best of our knowledge claim metal oxide to reoxidation ability, that is fundamental to understand catalytic activity process.

In this work, CuO , Co_3O_4 and Fe_2O_3 were prepared by calcination of their respective nitrates. The catalysts were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), programmed hydrogen reduction temperature (H_2 -TPR) and diffuse reflectance spectroscopy in the ultraviolet and visible region (DRS UV–Vis). The catalytic reactions were evaluated on the SCC- CH_3CN between 100 and 600°C keeping the mass of the metal constant of catalysts and products were identified by a mass spectrometer coupled to reactor.

2 Materials and methods

2.1 Catalyst preparation

The catalyst samples containing CuO , Co_3O_4 and Fe_2O_3 were prepared by calcination using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Dynamic), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Scientific Exodus) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Vetec). All reagents were used as were purchased. The calcination was performed in muffle at 650°C for 2 h with heating rate of $10^\circ\text{C}/\text{min}$, in static air.

2.2 Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD), temperature-programmed reduction by hydrogen (H_2 -TPR), and diffuse reflectance spectroscopy in ultraviolet–visible region (UV–vis). XRD analyzes were performed by the powder method on a Rigaku X-ray diffractometer (MiniFlex 600) operating at 40 kV, 15 mA and $\text{CuK}\alpha$ radiation. The speed of the goniometer used was $2^\circ (2\theta)/\text{min}$, the angle ranging between 15 and $60^\circ (2\theta)$. The crystal phases were determined by correlating the diffraction patterns with those in the X'Pert HighScore reference.

H_2 -TPR analysis was performed on a SAMP3 equipment (Termolab Equipment, Brazil) using 10 mg of sample and flow of 30 mL/min from a high purity mixture of 2 vol.% H_2 in Ar. The sample was heated up to 1000°C at $10^\circ\text{C}/$

min and the hydrogen consumption was monitored by a thermal conductivity detector. A trap was used to remove the water stemming from the reduction before the gas of the reactor outlet was sent to the TCD.

The diffuse reflectance data were monitored in the range of 200–800 nm using an UV–Vis spectrophotometer (Shimadzu UV 2700). BaSO₄ was used as reference material. Before the measurement, the samples were dried at 120 °C for 2 h to remove the water molecule or OH groups. The diffuse reflectance data were obtained directly from the spectrometer and converted to the Kubelka–Munk function, $F(R)$, using the Eq. (1), where R is reflectance.

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

The average particle size (τ) was calculated by the Debye–Scherrer equation (Eq. 2), considering the spherical geometry and using XRD reflection of CuO ($2\theta = 38.7^\circ$) Co₃O₄ ($2\theta = 36.9^\circ$) and Fe₂O₃ ($2\theta = 33.2^\circ$).

$$\tau = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where k is shape factor (0.9), λ is X-ray wavelength, β is line broadening from extra peak width half peak height and θ is the Bragg angle.

2.3 Catalytic tests

The activity of CuO, Co₃O₄ and Fe₂O₃ catalysts was evaluated in the selective combustion reaction of acetonitrile (CH₃CN–SCC) using a quartz wool-type “U” reactor fed with continuous flow of 50 mL/min of a mixture containing 2.8 vol.% CH₃CN in synthetic air. It was used 8.6 mg of metal in the sample and the reactor operated at atmospheric pressure and the reaction temperature was varied from 100 to 600 °C. The reactor was coupled in line to a mass spectrometer (THERMO) for gas analysis: N₂ ($m/z = 28$), O₂ ($m/z = 32$), H₂O ($m/z = 18$), HCN ($m/z = 27$), NO + N₂O ($m/z = 30$), NH₃ ($m/z = 17$), CH₃CN ($m/z = 41$) and CO₂ ($m/z = 44$). Conversion of CH₃CN was calculated through Eq. (3).

$$\text{Conversion (\%)} = \left(\frac{\text{CH}_3\text{CN}_{(\text{in})} - \text{CH}_3\text{CN}_{(\text{out})}}{\text{CH}_3\text{CN}_{(\text{in})}} \right) \times 100 \quad (3)$$

3 Results and discussion

The XRD patterns of the catalysts in Fig. 1 showed all the peaks characteristic of the crystalline structures found in the literature for CuO (PDF 45-0937), Co₃O₄ (PDF

Fig. 1 XRD patterns of CuO, Co₃O₄ and Fe₂O₃ catalysts. Peaks relating to copper oxide (o), zinc oxide (*), cobalt oxide (■) and iron oxide (+)

Table 1 Crystallite size of catalysts

Catalyst	Crystallite size (nm)*
CuO	20.0
Co ₃ O ₄	14.0
Fe ₂ O ₃	21.3

*Obtained by Debye–Scherrer equation

01-1152) and Fe₂O₃ (PDF 01-1053) [22–24]. As expected from the copper nitrate decomposition, the CuO catalyst exhibited all characteristic peaks of copper oxide with monoclinic crystal system at $2\theta = 32.4, 35.5^\circ, 38.6^\circ, 48.7^\circ, 53.4^\circ$ and 58.1° . No evidence of Cu₂O peaks (PDF 35-1091) was observed by XRD and the peak at 36.2° was attributed to small amount of ZnO (PDF 03-0888) of sample holder. In agreement with the literature [25], Co₃O₄ catalyst showed peaks relative to Co₃O₄ crystalline phase with cubic symmetry at $2\theta = 31.2^\circ, 36.9^\circ, 38.4^\circ, 44.8^\circ$ and 59.2° . XRD patterns of the Fe₂O₃ catalyst shows characteristic peaks of hematite crystalline phase (α -Fe₂O₃) with rhombohedral symmetry at $2\theta = 33.2^\circ, 35.7^\circ, 40.8^\circ, 43.7^\circ, 49.5^\circ, 54.1^\circ$ and 57.3° .

The average crystallite size for CuO, Co₃O₄ and Fe₂O₃ is estimated between 14 and 21 nm (Table 1). All catalysts showed nanoparticle formation, however, the CuO and Fe₂O₃ crystallite size were very close and Co₃O₄ had smaller crystallite size about 14 nm [26]. These nanoparticles should have better redox properties and exhibit greater activity for oxidation reactions.

Fig. 2 H_2 -TPR profiles of CuO, Co_3O_4 and Fe_2O_3 catalysts

Figure 2 shows all H_2 -TPR profiles of the CuO, Co_3O_4 and Fe_2O_3 catalysts. According to the literature [27], the reduction of CuO occurs by one-step ($Cu^{2+} \rightarrow Cu^0$) and two-step ($Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$) mechanisms. Note that CuO exhibited no clear splitting of reduction peak in two peaks. However, the single CuO peak can be deconvoluted in a peak at 304 °C and another peak at 356 °C, attributed reductions of Cu^{2+} to Cu^{1+} and Cu^{1+} to Cu^0 , respectively. The areas correspondences of both peaks confirm the model of a two-step reduction process. On the other hand, Co_3O_4 has spinel-type structure with crystal chemical formula $Co^{2+}Co_2^{3+}O_4$, where Co^{2+} ions occupy the tetrahedral positions and Co^{3+} ones are in the octahedral positions [28]. Co_3O_4 reduction has beginning with a peak at 270 °C, which is attributed to reduction of $Co^{3+} \rightarrow Co^{2+}$, i.e., Co_3O_4 to CoO. Then, once CoO clusters forms the reduction reaction of CoO to Co^0 occurs with a peak at 346 °C. Finally, CoO particles bulk is reduced to metallic cobalt in the peak at 410 °C.

Figure 2 shows also that the reduction of Fe_2O_3 occurs in more than one stage. The first peak corresponds to the reduction of Fe_2O_3 to Fe_3O_4 occurs around 295 °C (Eq. 4). The reduction of Fe_3O_4 to Fe^0 can be observed in the range of 330–700 °C, which can occur via FeO ($Fe_3O_4 \rightarrow FeO \rightarrow Fe^0$) [29]. The reduction peaks at 438 and 570 °C corresponds to the simultaneously reduction of $Fe_3O_4 \rightarrow FeO \rightarrow Fe^0$, according to Eqs. 5 and 6. Briefly the Fe_2O_3 reduction occurs in three overlapping stages and the entire process was completed above 700 °C. Equation 4 shows that the first reduction of Fe_2O_3 is thermodynamically favorable at low temperatures ($\Delta G = -33.0 \text{ kJ mol}^{-1}$), the second and third reduction event happened in high temperatures, that is associated with Eqs. 5 and 6 [29].

The further information on the species present in the CuO, Co_3O_4 and Fe_2O_3 catalysts were studied by UV–Vis spectroscopy, as shown in Fig. 3. UV–Vis absorption spectra of catalysts were deconvoluted using a gaussian fit treatment; this makes it clear electronic transitions of each solid. Catalysts spectra shows a broad and strong absorption the UV–Vis in 350–750 nm range for the three catalysts, it may be a strong color consequence of them. Some studies have presented that nanoparticle size effect may influence the band gap of semiconductors, which generally decrease when the size of the nanoparticle increases [30]. Furthermore, band gap values almost trends zero electron-volt when nanoparticles are found in a big size or a thick film [31]. In our case, it does not clear to recognize absorption region responsible for band gap transition for CuO and Co_3O_4 catalysts, even using Tauc function plot [6, 32]. In general, band gap energy overlay the absorption range 200–600 nm of the spectrum, whose region is very well delimited for a charge transfer energy band between

Fig. 3 UV–Vis absorption spectra for CuO, Co_3O_4 and Fe_2O_3

ligand-metal. Relationship between nanoparticle size and band gap values has also been described for different sort of transition metal oxides [33]. This work does not intend goes further deeply about nanoparticle size, only it signs a possibility according to results found. Here, we might infer about crystallite of Cu, Co and Fe oxides has nano size, who was showed by Scherrer equation, although UV-Vis absorption spectra lead an interpretation of big size particle behavior structure. It is important let clear that crystallite size does not mean same particle size [7, 30]. While it does not precisely size particle of three catalyst, is import recognize that data shows near estimates between them, who catalytic contributions may come from only electronic environment properties of each metal. UV-Vis spectroscopy is a powerful characterization method to study the coordination geometry of the materials.

Concerning about electronic transitions found over absorption UV-Vis spectra (Fig. 3), Fe_2O_3 present a prominent peak at 557 nm is a characteristic feature of Fe^{3+} ion in octahedral symmetry, it also sees bands deconvoluted at 410 nm and spectrum region above 800 nm, that confirming ferric ion [34, 35]. UV-Vis absorbance spectrum for CuO catalyst present peaks like 303 and 682 nm, who are related electronic transitions in CuO crystalline phase. It also shows a peak at 588 nm that some studies explain Cu^+ presence due to Cu_2O assignment [31]. Co_3O_4 has a black color and presented a characteristic flat band spectrum (Fig. 3), which is characteristic of dark colored materials. Although the Co_3O_4 spectrum is quite remarkable, the ordered axis of the absorption spectrum was enlarged for better visualization of the peaks. Between 450 and 750 nm, this spectrum displays three absorption peaks (478, 559, and 663 nm), which can be unambiguously assigned to the transition of Co^{2+} ions in tetrahedral environments. Moreover, a broad band in the UV region centered at 255 nm is also observed. This has been assigned to a low-energy charge transfer between the oxygen ligands and central Co^{2+} ion in tetrahedral symmetry. Another broad absorption was centered at 345 nm, which was assigned to Co^{3+} species. It could be found in the literature that Co^{3+} was usually obtained through a heating treatment such as calcinations [36].

Figure 4 shows acetonitrile conversion on CuO, Co_3O_4 and Fe_2O_3 catalysts as function of the reaction temperature. These oxides showed high catalytic activity in the reaction of acetonitrile combustion; whose activity order follows for $\text{Co}_3\text{O}_4 > \text{CuO} > \text{Fe}_2\text{O}_3$. Conversion of acetonitrile started in temperatures at 264 °C, 270 °C and 350 °C for the Co_3O_4 , CuO, and Fe_2O_3 catalysts, respectively. Co_3O_4 exhibited better catalytic activity at lower temperatures, where at 300 °C almost 55% of all acetonitrile had already been converted, and total conversion can be seen at 570 °C. CuO showed catalytic activity similar

Fig. 4 Acetonitrile conversion over CuO, Co_3O_4 , Fe_2O_3 with 8.6 mg of metal in the sample

to Co_3O_4 at low temperatures, and at 312 °C, 54% of acetonitrile had already been converted and above 595 °C it is already possible to have total conversion. Fe_2O_3 was the catalyst with the lowest catalytic activity between them in lower temperature, 50% acetonitrile was converted at 378 °C and 98% acetonitrile converted at 600 °C.

Catalysts performance can be related with thermodynamic stability of crystalline structure of metal oxides used, as verified by H_2 -TPR, we can see that the reducibility of the cations increases in the order $\text{Fe}^{3+} < \text{Cu}^{2+} \sim \text{Co}^{3+}$ [37].

Note that both CuO and Co_3O_4 were found two oxidation number states, also corroborated by UV-vis DRS analysis, that may suggest important role with redox process on acetonitrile combustion reactions. Possibility of coexistence both sites in structure of catalyst in room temperature lead to stability crystalline phase and smaller barrier energy for the reaction. However, some authors showed Cu activity in catalytic combustion of acrylonitrile using different zeolitic supports [38, 39]. It is very known that great area surface may favor catalytic activity owing to high level of metal dispersed, and they also cited a possibility who main role of metals in catalytic combustion there is involved to redox ability, more important than the specific surface area.

In this work we concern to describe important phenomena between two oxidation states in the catalysts, which is helping to understand the activity. The Cu and Co oxides had a good reduction sign through H_2 -TPR analysis, which was performed in low temperature and without broad band compared Fe_2O_3 catalyst. These quite good results are related with potential catalytic activity, who were corroborated goes through acetonitrile conversion in lower temperatures (~ 300 °C).

On the other hand, is interesting to understand Fe_2O_3 catalyst redox behavior, who may relate to crystalline phase thermodynamic stability aspects in react conditions, then in the second step, the catalytic activity with acetonitrile become clearer. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) crystalline phase present in Fe_2O_3 catalyst has only Fe^{3+} ion in structure which is possible change oxidation number during reaction to Fe^{2+} ion. Magnetite phase (Fe_3O_4) contain both iron (II) and (III) and is very common to obtain by synthetic process, but the electronic and structural stability are sensible dependent of the chemical environment. For example, the ferrimagnetic iron-oxide phases (Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$) transform to stable $\alpha\text{-Fe}_2\text{O}_3$ phase between 200 and 350 °C. Fe_3O_4 first transforms to $\gamma\text{-Fe}_2\text{O}_3$ phase between 200 and 250 °C, the $\gamma\text{-Fe}_2\text{O}_3$ phase then transforms to $\alpha\text{-Fe}_2\text{O}_3$ between 300 and 350 °C [40, 41]. These transformations are often observed to occur in nature, but very slowly depending on the temperature and other environmental conditions. The fact is, Fe_2O_3 catalyst has small barriers of activity compared to others catalysts here studied, due to thermodynamic aspects to change their crystalline phase, this also influence to changes in oxidation number of the $\alpha\text{-Fe}_2\text{O}_3$. The equilibria of both oxidation states are very important in redox process with Fe_2O_3 that is dependent of temperature, oxygen concentration and electron donor species present like acetonitrile or some byproduct from reaction.

Some authors have discussed about sensibility of Co^{2+} and Fe^{2+} in presence of low pressure of O_2 . Under the oxidizing conditions Co_3O_4 preserves the spinel structure, in contrast to the case for other spinels. It may be, however, faintly disordered in the surface region by formation of the $\text{Co}^{4+}(\text{h}\cdot)$ defects upon interaction with oxidants (O_2 or N_2O). As a result, a $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple associated with the octahedral core is established, this fact for example, playing a vital role in nitrous oxide decomposition. Fe_3O_4 is gradually transformed into the corresponding sesquioxides under such conditions, showing that the Fe^{2+} state is unstable even at $p\text{O}_2/p_0 = 0.02$. As a result, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pairs in the spinel host cannot operate in a sustainable way in the catalytic processes involving oxygen as a reactant [37]. Another important factor has been considered is nanocrystal size, mainly to Co_3O_4 that showed lower crystallite size (14.0 nm). We suggest high possibility Co_3O_4 catalyst present more expose terrace, edge and corner atoms compared with CuO catalyst (crystallite: 20.0 nm), who put cobalt catalyst in the best catalytic activity.

Considering the products formed (Fig. 5), were observed high selectivity toward N_2 and CO_2 for three catalysts used and few amounts of another nitrogen-containing by-products as NO, NO_2 , HCN, N_2O and NH_3 in SCC- CH_3CN . The formation of CO_2 , the product of the oxidation reactions of organic compounds, was verified and at lower temperature

there is greater conversion to CO_2 , according to the formed currents for the CuO, Co_3O_4 and Fe_2O_3 catalysts. Concomitant with the formation of CO_2 ($m/z = 44$) another product that can be formed, in SCC- CH_3CN , the nitrogenous compound N_2O (nitrous oxide) that has the same molecular mass as CO_2 .

Studies have explained that N_2 yields constitute another important indicator for the catalytic performances [38]. The mechanism of reaction is correlated with the electro-withdrawal ability of the cationic sites from the N lone pair upon the adsorption of CH_3CN . Reports concerning the coordination chemistry, proposed that the acetonitrile can be adsorbed on the metal atomic center of the catalyst through two manners: an end-on interaction via the nitrogen lone-pair orbital or the side-on interaction via π of $\text{C}\equiv\text{N}$ group [39]. There were reported that the prerequisite of N_2 formation come through acylamino (CONH_2) intermediary [42].

The acetonitrile adsorbs over metal surface and then some complex reactions happen that are delineated by redox process. In the literature was described the mechanism reaction with iron catalyst [42], that is also possible to extend to metals (M) that have $\text{M}^{2+}/\text{M}^{3+}$ redox couple like cobalt catalyst, whose achieved high activity near 300 °C.

Going further to mechanism supported by other studies, after acetonitrile bonding's cleavage over surface, hydrolysis process in which CONH_2 is formed through nitrile (CN) hydrolysis (Fig. 6), then reacted with atomic O^- to get $\text{ONH}_2^- - \text{Co}^{3+}$ species, subsequently, these species quickly undergo hydrogen redistribution that H atom was connected to N atom neighbor linked with O atom, forming $\text{HONH}^- - \text{Co}^{3+}$ species. The hydroxyl was immediately desorbed from surface leaving $\text{NH}^- - \text{Co}^{3+}$ species on the surface. Subsequently, another atomic O^- react with N atom achieve $\text{O}^- \text{NH} - \text{Co}^{3+}$ species to obtain $\text{HON}^- - \text{Co}^{3+}$ species. Finally, the $\text{N}^- - \text{Co}^{3+}$ interact with another N atom to get the end product of N_2 after hydroxyl was stripped.

Through a possible mechanism reaction presented, the redox process makes vital importance for the reaction to occur. Other undesirable by-products were observed in low current of NO, NO_2 , NH_3 and HCN, due to elements contain in acetonitrile and potential bonding cleavage, there are possible detected them arranged as other different molecules [43, 44]. The high selectivity to N_2 is achieved by contributions of crystallite size, metal redox couple and energy barrier involved, but fundamental process is leaded if redox ability in high temperature can be performed according to stability crystal phase can work.

Fig. 5 Catalytic performance as function of temperature in the SCC-CH₃CN over CuO, Co₃O₄, Fe₂O₃. Conditions: 2.8% CH₃CN, 8.6 mg of metal in the sample

4 Conclusion

CuO, Co₃O₄ and Fe₂O₃ catalyst were characterized by XRD, H₂-TPR and DRS-UV-Vis which are possible to identify their crystalline structures. Presence of two valence sites in

catalyst like Co₃O₄ and CuO showed significant catalytic activity leading to oxidation loop by catalyst to close. The redox process showed high selective catalytic combustion of acetonitrile with high selectivity to N₂ through Co₃O₄ catalyst, who also report with shorter nanocrystal size. All

Fig. 6 Metal redox effect scheme for N_2 selectivity

catalysts showed, even in less producing, of nitrogen-hazardous compounds like N_2O , NO , NO_2 and HCN . Higher CO_2 formation was observed for three catalysts. The crystalline phase and their stability are the major factor to decide best catalyst to use. In some works, about SCC the redox processes involved have not received too much attention as required.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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