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N_2O decomposition coupled with ethanol oxidative dehydrogenation reaction on carbon-supported copper catalysts promoted by palladium and cobalt

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Abstract

Nitrous oxide (N_2O) is one of the most potent greenhouse gases which contributes to ozone layer depletion. The abatement and value-added utilization of waste N_2O are thus an important task. In this work, Cu/C, Pd-Cu/C, Pd-Co-Cu/C and Co-Cu/C catalysts were prepared and tested in the oxidative dehydrogenation of ethanol in the presence of N_2O. All catalysts were active and selective to acetaldehyde above 150 °C and the Co-Cu/C catalyst performed the best. The role of the α-oxygen obtained from the N_2O decomposition was also investigated.

Keywords: N_2O decomposition; Ethanol oxidative dehydrogenation; Co-Cu/C

1. Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas and contributes to ozone layer depletion. The emissions related to the production of adipic acid have been reported to correspond to up to 10% of the growth in atmospheric N_2O. This has prompted the development of several abatement technologies based mainly on the catalytic decomposition, however, value-added utilization of waste N_2O has been envisaged [1,2].

N_2O is relatively unreactive but oxidizes certain low-valence transition metals even at room temperature [3]. At moderate temperatures, a charge donation from a catalytic site into the N_2O anti-bonding molecular orbitals leads to decomposition, giving N_2 and a highly active form of adsorbed oxygen. This specific and reactive species was called α-oxygen and it inserts into C–H bonds, allowing the direct oxidation of organic molecules, such as benzene to phenol [2,4].

Acetaldehyde is an important intermediary in organic syntheses and is obtained as a product of catalytic ethanol partial oxidation. As shown in FTIR studies, ethanol is dissociatively adsorbed producing hydrogen and adsorbed ethoxide intermediary that further dehydrogenate producing acetaldehyde [5].

The catalytic oxidation of ethanol has generally been investigated in order to develop catalysts that maximize products, such as acetaldehyde or acetic acid and minimize production of deep oxidation reactions. Massive and supported oxides of Mo, Fe, Co, Ni, Cu, Ag and Au are among the catalysts reported in the current literature on the partial oxidation of ethanol [6]. Although copper oxide catalysts were reported as active and selective, they are quickly deactivated by sintering [7]. The use of appropriate support or the addition of a metal promoter might be considered an alternative to improve the copper oxide dispersion, thus avoiding or limiting the sintering.

Alumina-supported noble metals, such as Rh, Pd and Pt, have been reported [8] as highly active for N_2O decomposition. Thus, the addition of palladium has been used both to limit the copper oxide sintering and to promote N_2O decomposition.

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Cobalt-exchanged zeolites showed higher hydrothermal stability than copper-exchanged zeolites, maintaining high N_2O decomposition activity [9].

In this work, carbon-supported copper catalysts, promoted with Pd and Co — Cu/C, Pd-Cu/C, Pd-Co-Cu/C and Co-Cu/C — were prepared, characterized and evaluated in the oxidative dehydrogenation of ethanol using N_2O as an oxidant agent, in order to investigate the production of acetaldehyde in the presence of α-oxygen.

2. Experimental

A S-Sorb 12 Cu/C (10% Cu, 995 $m^2 g^{-1}$) catalyst supplied by Calgon Carbon Corporation was used as starting material for catalyst preparation. Catalysts containing Co and/or Pd were prepared by impregnation, using aqueous solutions of palladium chloride(II) (Aldrich, 99.99% purity) and cobalt nitrate(II) (Merck, 99.99% purity). The catalysts were dried at 60 °C in a vacuum oven and then calcined at 300 °C, under 60 mL min^{-1} air flow, for 4 h. The tri-metallic catalyst was prepared by consecutive impregnation of the Cu/C base catalyst with aqueous solutions of the precursor cobalt nitrate followed by palladium chloride. Each impregnation was followed by removal of solvent under vacuum (60 °C). Finally, the catalyst was calcined at 300 °C, under 60 mL min^{-1} air flow, for 4 h.

The chemical composition of the prepared catalyst and precursors was determined using a N_2O/acetylene flame atomic absorption spectrometer Varian model SpectrAA220; the samples were dissolved in concentrated nitric acid (Merck, assay 70%) prior to the analysis.

Thermo gravimetric analyses of the catalysts were carried out in a TGA-50 Shimadzu, using synthetic air, nitrogen or nitrous oxide flow in order to investigate the gasification of the carbon support. The heating rate used was 10°/min and the gas flow was 50 mL min^{-1}.

X-ray diffraction patterns were collected using a Shimadzu XRD6000 and Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) and the following experimental conditions were used: 2θ range = 10–80°, step size = 0.02° and time per step = 4.80 s. The powder samples were analyzed without further treatment.

Surface area of the samples was measured by the N_2 adsorption technique (BET method) using ASAP 2010 V4 apparatus.

TPR experiments were carried out using a home built apparatus with a thermal conductivity detector, under a 30 mL min^{-1} flow of 5% H_2/N_2, going from 30 to 600 °C and with a heating rate of $\beta = 10$ °C min^{-1}.

FTIR spectra of adsorbed N_2O and ethanol were carried out in a Jasco Valor III spectrometer, with an MCT detector, using self-supported catalyst wafers (10–14 mg), previously treated at 200 °C for 1 h.

Reaction experiments were carried out using a continuous flow U-tube micro-reactor which operated at ambient pressure in the temperature range of 100–450 °C, 16,500 h^{-1} space velocity and CH_3CH_2OH/N_2O molar ratio of 25.5. The feed gas containing 8% N_2O in He was passed through a glass saturator containing ethanol at controlled temperature (40 °C). Before testing, the catalysts (0.1 g, 60–80 mesh) were treated in flowing nitrogen at 200 °C, for 2 h. Feed and product gases (ethanol and acetaldehyde) were analyzed with the aid of gas chromatography, using a flame ionization detector and a Porapak N column. The experiments for N_2O decomposition were carried out using the same apparatus, but the feed and product gases were analyzed with a thermal conductivity detector, using a Porapak N and a 5 Å molecular sieve columns, as described by Mascarenhas and Andrade [1].

3. Results and discussion

Table 1 presents the composition and surface area of all catalysts used in this work. The base catalyst, Cu/C, showed the highest surface area and a significant loss of surface area is observed in the palladium-promoted catalyst. As observed by Tseng et al. [6], acid treatments may cause loss of surface area and pore volume of activated carbon, due to the structure sintering caused by reaction with some oxygenated surface species. This probably occurred during palladium impregnation, as the $PdCl_2$ solution was prepared with pH near zero.

The cobalt-containing catalysts also showed a loss of surface area compared to the base Cu/C catalyst, but not so markedly. This fact may be explained by the same argument above, the loss of surface area was to a lesser degree because the cobalt nitrate solution used for impregnation was only slightly acidic (pH 5). The presence of metal precursors on the carbon surface may also cause a loss of surface area due to obstruction of the pores by the oxides formed by calcination [6].

The presence of many oxide phases was confirmed by X-ray diffraction (Fig. 1). CuO (monoclinic) was present in the Cu/C and Co-Cu/C catalysts. Co_3O_4 was detected in both Co-containing catalysts. Metallic palladium was observed in both Pd-containing catalysts, in spite of the calcination at 300 °C. Mixed oxides phases, such as $Co_2O_3{\cdot}CuO$, $Cu_{3.86}Pd_{0.14}O_3$ and $CuPdO_2$, may be present in some catalysts, as indicated in Fig. 1. These phases were generated from the original CuO phase, this explains why CuO monoclinic was detected in very small quantities in these catalysts.

The reducibility of the oxide phases was compared using TPR (Fig. 2). All catalysts presented a complex TPR profile

Table 1
Composition and surface area of the prepared catalysts

Sample	Composition (wt%)			Surface area ($m^2 g^{-1}$)
	Pd	Co	Cu	
Pd-Cu/C	1.08 ± 0.02	0.00	9.38 ± 0.03	632.00
Pd-Co-Cu/C	1.17 ± 0.02	0.08 ± 0.02	9.99 ± 0.01	851.00
Co-Cu/C	0.00	0.09 ± 0.02	9.89 ± 0.02	986.92
Cu/C	0.00	0.00	9.98 ± 0.02	995.07

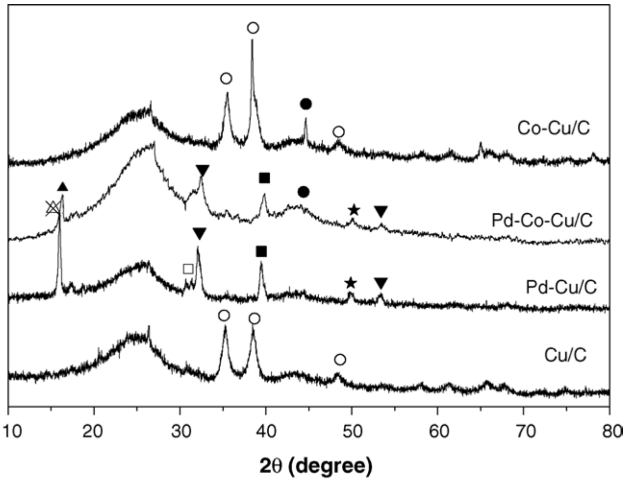


Fig. 1. X-ray diffraction patterns of the calcined catalysts. *Legend:* (○) CuO; (□) PdO; (▲) Co_2O_3·CuO; (▼) $CuPdO_2$; (☒) not identified; (★) $Cu_{3.86}Pd_{0.14}O_3$; (●) Co_3O_4; (■) Pd.

given the complex chemical nature of the carbon surface [10]. Pure CuO can be expected to reduce at around 240 °C [7]; supported CuO may be reduced at higher temperatures depending on the particle size and its interaction with the support. Moreover, the presence of other metals, such as Pd and Co, may influence the CuO phase reduction, which normally takes place in two stages, Cu(II) to Cu(I) and finally to metallic copper. The presence of cobalt in the Co-Cu/C catalyst, despite the low Co content, facilitated the Cu(II) reduction, as the first peak, ascribed to CuO reduction, was located at around 185 °C, the lowest reduction peak compared to the other catalysts (Fig. 2). The presence of mixed oxides phases, as seen in XRD and the complex carbon surface, on the other hand, make it difficult to evaluate the TPR profiles and consequently, the influence of palladium in the reducibility of the catalysts. The Pd-Co-Cu/C catalyst showed a reduction peak of around 400 °C, generally ascribed to the reduction of Co^{3+} species [11]. These species may be present in this catalyst, as observed using the XRD technique (Fig. 1).

In the ethanol catalytic oxidation reaction, better conversions were obtained in oxidative atmosphere [4,12], but the support carbon may be consumed [11]. In this work, the stability of the catalysts was checked using TGA in O_2, N_2 and N_2O atmospheres. The results are presented in Fig. 3a–c, respectively. A loss of adsorbed water was observed in all experiments and all catalysts were quite stable in N_2 atmosphere. However, an important loss of mass was observed at temperatures higher than 300 °C in O_2 atmosphere and higher than 400 °C in N_2O atmosphere for all catalysts. The Co-Cu/C catalyst exhibited the highest thermal stability, in O_2 atmosphere, when compared to the other catalysts (Fig. 3a). The TGA experiments showed that N_2O may be used below 400 °C without significant loss of mass of the catalysts.

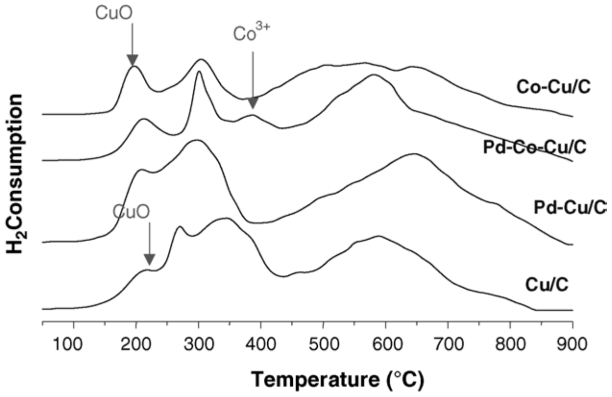


Fig. 2. TPR profiles for the calcined catalysts.

Fig. 4 shows the conversion of ethanol to acetaldehyde (CO_2 and H_2O were not detected) in N_2 and N_2O atmospheres, using the base Cu/C catalyst, in the temperature range from 350 to 450 °C. Even in the N_2 atmosphere, the formation of acetaldehyde is observed, but the use of N_2O atmosphere roughly doubles the ethanol conversion.

Fig. 5 presents the conversion of ethanol to acetaldehyde in N_2O atmosphere, using all the prepared catalysts, in the same operational conditions. The Co-Cu/C and Cu/C catalysts exhibited the best performances. CuO is known to be a good catalytic phase for alcohol oxidative dehydrogenation, its performance is related to both the $Cu^0/Cu^+/Cu^{2+}$ redox cycles [13] and the presence of loosely bound oxygen on the surface [14]. CuO was actually the main phase detected by XRD in the Co-Cu/C and Cu/C catalysts, which performed the best (Fig. 1).

The order of activity in the N_2O decomposition experiments with same catalysts, from 300 to 450 °C (Fig. 6), was the same as observed above: the Co-Cu/C catalyst had the best performance, followed by the Cu/C, Pd-Co-Cu/C and Pd-Cu/C catalysts. The conversion of all catalysts increased continuously as the reaction temperature increased, in spite of the loss of mass observed at temperatures higher than 400 °C (Fig. 3c). These results indicate the important role played by N_2O decomposition for the overall reaction. Cruz et al. [9] observed the excellent performance of Cu-ZSM-5 and Co-ZSM-5 catalysts in the N_2O decomposition reaction.

In order to better understand these reaction mechanisms, certain ‘‘in situ’’ FTIR experiments were performed. Even in N_2 atmosphere, acetaldehyde is formed from ethanol at temperatures above 150 °C, using the Pd-Cu/C catalyst (Fig. 7). Ethoxides species were detected on the catalyst surface, confirmed by the bands at 2989 cm^{-1} (ν_{ass} CH_3), 2902 cm^{-1} (ν_{sim} CH), 1394 cm^{-1} (δ_{sim} CH_3), monodentate species at 1065 cm^{-1} and bidentate species at 1057 cm^{-1} (ν C=O). The presence of acetaldehyde was confirmed by the large band at around 1760 cm^{-1}, observed above 150 °C and ascribed to axial deformation of the C=O bond in this molecule [7,9] (Fig. 7).

A very similar experiment, except in N_2O atmosphere (Fig. 8), showed the same species above and another peak at

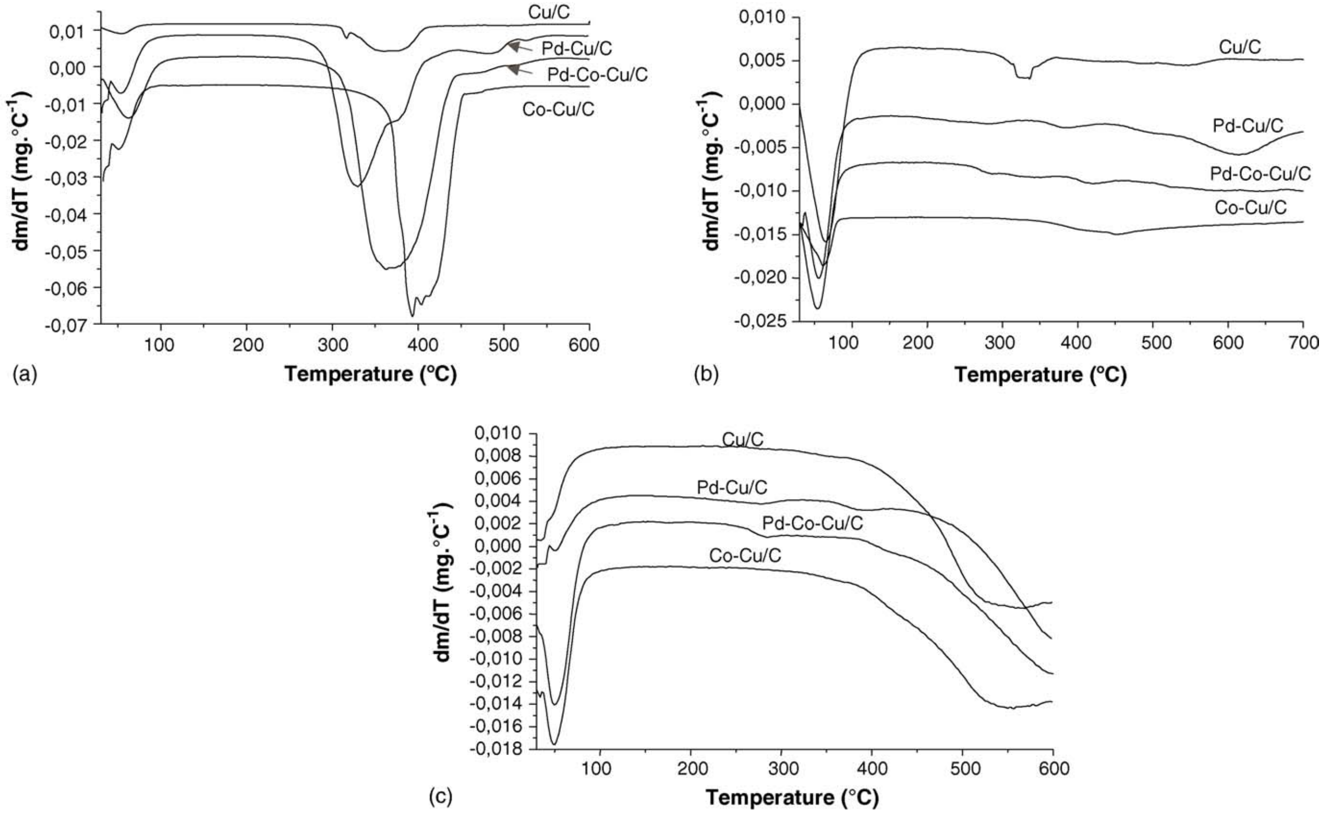


Fig. 3. Thermal and chemical stability of the catalysts using TGA in flowing: (a) O_2; (b) N_2; (c) N_2O.

around 2240 cm^{-1}, ascribed to N_2O adsorbed near an oxygen atom generated by the N_2O decomposition reaction, named oxygen α [15], also observed by TPD-MS [16].

Another experiment was performed using N_2O without ethanol and using the same catalyst at 100 °C (Fig. 9). The same peak at around 2240 cm^{-1} was observed, confirming the α-oxygen formation from N_2O decomposition.

Based on these results, the following simplified mechanism was proposed for the ethanol oxidation reaction coupled with N_2O decomposition reaction (Scheme 1), with some steps according to Idriss and Seebauer [17].

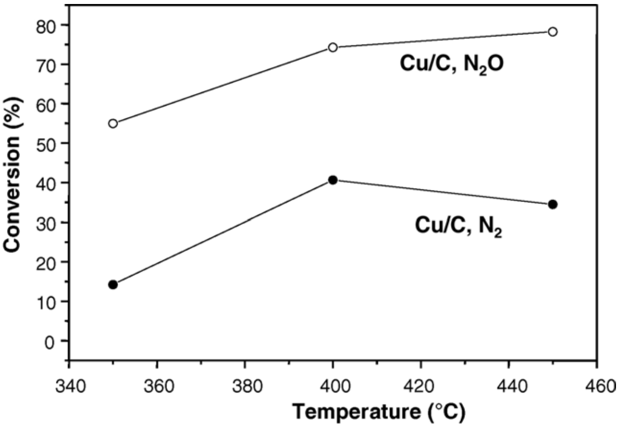


Fig. 4. Conversion of ethanol to acetaldehyde over Cu/C catalyst as a function of chemical environment (N_2O and N_2) and temperature.

These diagrams show the need for reducible and reoxidizable phases to perform these reactions. N_2O has an important role in the regeneration of the surface sites [7] and also in the generation of the active α oxygen. In N_2O adsorption and decomposition mechanisms (step 4), the electron transfer from the surface metal ion to the N_2O molecule is a crucial step. The catalytic reaction requires the oxidation of partial reduced sites as well as the reduction of the ion from the high oxidation state to the original one [18].

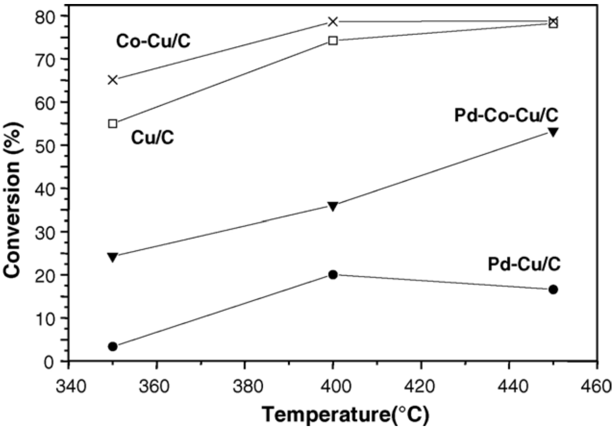


Fig. 5. Conversion of ethanol to acetaldehyde in the presence of N_2O as a function of the reaction temperature over Pd-Co-Cu/C, Pd-Cu/C, Co-Cu/C and Cu/C catalysts (CH_3CH_2OH/N_2O = 25.5; SV = 16,452 h^{-1}).

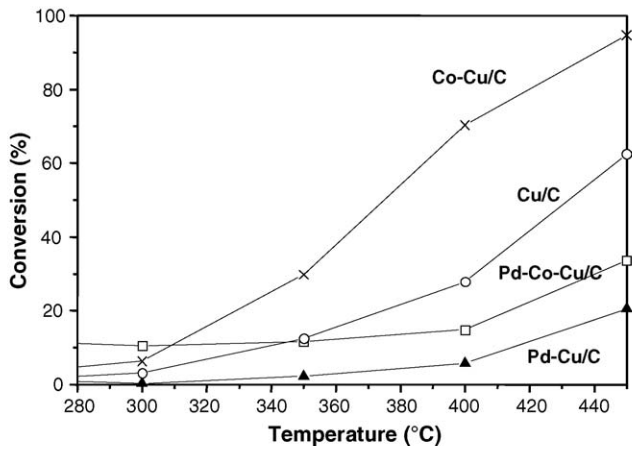


Fig. 6. N_2O decomposition reaction as a function of the temperature over Pd-Co-Cu/C, Pd-Cu/C, Co-Cu/C and Cu/C catalysts.

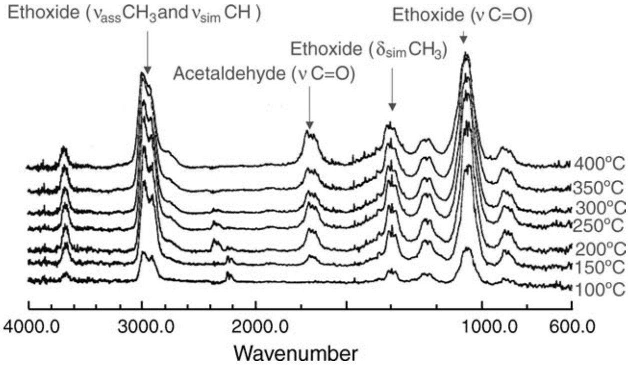


Fig. 7. In situ FTIR spectra of adsorbed EtOH over Pd-Cu/C as a function of the temperature in nitrogen atmosphere.

Among the oxide phases detected by XRD (Fig. 1), Cu^{2+}, Pd^{2+}, Co^{2+} and Co^{3+}, the cobalt species are better able to restore the original oxidation state, from the high oxidation state Co^{3+} as compared to palladium and copper. However, this fact alone fails to explain the best performance of cobalt-modified Cu/C catalyst, related to the palladium-modified Cu/C catalyst. Moreover, there is insufficient thermodynamic data on mixed oxides phases, also detected by XRD analysis.

From the kinetic point of view, alumina-supported CuO catalysts exhibited low activation energies for the N_2O decomposition reaction, giving high conversion values above 330 °C [19], in agreement with the results obtained in this work.

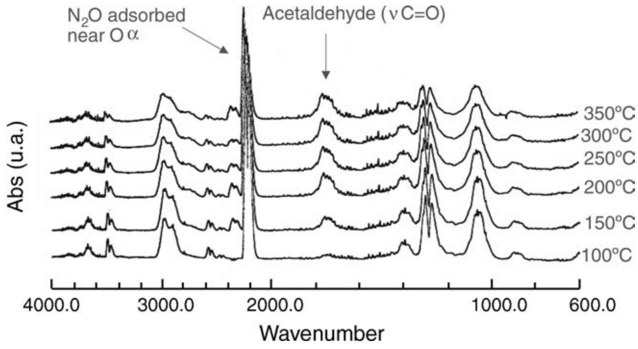


Fig. 8. In situ FTIR spectra of adsorbed EtOH over Pd-Cu/C as a function of the temperature in N_2O atmosphere.

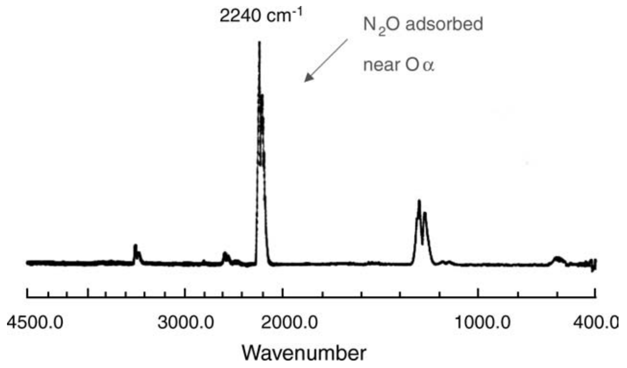
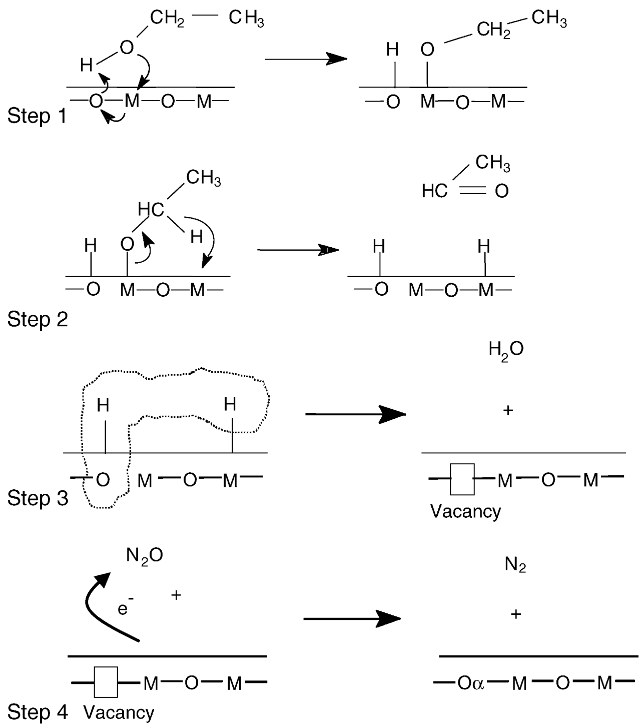


Fig. 9. In situ FTIR spectra of the N_2O decomposition over the Pd-Cu/C catalyst at 100 °C.

The presence of cobalt increased the activity of the catalysts Co-Cu/C and Pd-Co-Cu/C, as compared to the Cu/C and Pd-Cu/C catalysts, respectively. This effect is probably related to the redox cycles, as discussed above. In spite of this, Pd-Co-Cu/C exhibited lower conversions than the Co-Cu/C catalyst in both reactions and this fact may due to the formation of less reactive phases, presumably, the mixed oxides detected by XRD (Fig. 1).



Scheme 1. Simplified mechanism for the ethanol oxidation reaction coupled with N_2O decomposition reaction. Step 1: formation of surface ethoxides species by heterolytical dissociation of ethanol. Step 2: formation of acetaldehyde from the ethoxides species (rate determining step [11]). Step 3: water formation. Step 4: reoxidation of the sites by N_2O decomposition.

4. Conclusion

The Cu/C, Pd-Cu/C, Pd-Co-Cu/C and Co-Cu/C catalysts exhibited significant activity, with a selectivity of around 100% to acetaldehyde, in the oxidative dehydrogenation of ethanol coupled with N_2O decomposition in the range of 150–450 °C. The Co-Cu/C and Cu/C catalysts performed the best, with conversions of around 80% at 450 °C, either in coupled or separate reactions.

The results suggest that the oxidative dehydrogenation of ethanol occurred via the formation of surface ethoxide species and this reaction is favored by the α-oxygen generated by the N_2O decomposition reaction.

The increase in the activity of cobalt-containing catalysts was a result of the ability of Co species to restore the original oxidation state, from the high oxidation state Co^{3+}, as compared to palladium and copper, but additional studies should be undertaken related to the mixed oxides phases observed in this work.

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