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Research Note

Hydroxylation/oxidation of benzene over Cu-ZSM-5 systems: Optimization of the one-step route to phenol

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Abstract

Cu-containing ZSM-5 materials were carefully prepared using a solid-state ion-exchange procedure to provide an outstanding performance in the direct gas-phase benzene oxidation to phenol using both oxygen and oxygen/hydrogen mixtures as oxidants. In particular, a ZSM-5 catalyst with a 100% modification level of copper (Cu/Al = 0.5) showed a phenol yield increasing with temperature up to 400 °C and approaching a high value of ca. 10%. The study shows that optimization of the phenol yield in the Cu-ZSM-5 system appears to be correlated with the appearance of size-limited Cu species, and that the presence of H_2 in the feed has beneficial/detrimental effects depending on the zeolite loading with Cu.

Keywords: Hydroxylation/oxidation of benzene; Phenol; Cu-ZSM-5; UV–visible spectroscopy; Raman spectroscopy

1. Introduction

Phenol is a versatile chemical used primarily in the formation of phenolic resins, as a solvent for petroleum refining, and in the production of nylon and other synthetic fibers. The well-known antiseptic properties of phenol promote additional industrial and medical applications. Most of the worldwide production of phenol (and also acetone) is now based on the "cumene process," a rather laborious, three-step reaction that has as main advantage the conversion of the two relatively inexpensive starting materials, benzene and propene, into the two (more) valuable chemicals phenol and acetone. However, its major drawback is that the overall economics of the process strongly depends on the demand of the acetone byproduct in the chemical market. This situation has prompted scientists to develop other methods for producing phenol from benzene, preferably via a single-step and free of co-product(s) reaction, which thus would be economically favorable.

Copper-containing zeolites drew much attention and were studied in detail after demonstrating their ability to catalytically remove NO from exhaust gases [1]. Their application in other reactions is apparently limited, however. Nevertheless, Tsuruya and co-workers [2–4] reported the use of Cu-ZSM-5 as a catalyst for the one-step oxidation of benzene to phenol using molecular oxygen as the oxidant. Several conditions of the reaction were optimized, and at 400 °C, the yield of phenol was 4.9% with ca. 30% selectivity. In this study, we made further efforts to develop the Cu ion-exchanged ZSM-5 system as an efficient catalyst for the one-step, environmentally friendly formation of phenol by direct oxidation of benzene, using molecular oxygen as well as an oxygen/hydrogen mixture. The use of copper as the active phase has significant advantages over current alternative catalysts based on iron; the latter requires the use of N_2O, a very toxic and global-warming related gas molecule, as an oxidant of the organic reactant [5–7]. Then safety and economic concerns motivate the use of the inert and cheap O_2 molecule instead of N_2O. In this report we describe the synthesis of the two copper-containing catalysts tuned to give, at specific reaction conditions, phenol as the only organic product of the reaction. We also explore maximizing the yield of phenol among the products of benzene oxidation at conditions under which other byproducts appear in the reactor outlet.

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Table 1
Main characterization results of the Cu-ZSM-5 systems

Catalyst	Si/Al	Modification degree by copper (%)	Cu/Al	Cu (wt%)	BET (m^2/g)
0.1Cu-ZSM-5	47.5	10	0.05	0.11	321
1.0Cu-ZSM-5	47.5	100	0.5	1.1	319

2. Experimental

The ZSM-5 sample was synthesized at the Institute of Industrial Chemistry, Warsaw, with a Si/Al ratio of 47.5 (100% crystallinity). The hydrogen form of zeolite ZSM-5 material was modified by introducing of Cu^{2+} ions using the contact-induced ion-exchange (solid-state ion-exchange) procedure [8]. The Cu-containing catalysts were obtained by mixing copper acetate (Merck, p.a.) with the H-form of zeolite, followed by calcination in a helium flow at 550 °C for 2 h. Table 1 summarizes the main physicochemical characteristics of the two Cu-ZSM-5 catalysts studied in this work. The Cu content of the materials is given by a number inserted before the symbol of the ion; for example, 1.0Cu-ZSM-5 refers to a ZSM-5 sample with the 100% modification level of copper. The amounts of Cu were calculated in proportion to aluminium content in the zeolite: 100% Cu → $1Cu^{2+}/2Al^{(-)} \rightarrow Cu/Al = 0.5$.

Two reactions leading to the direct, gas-phase conversion of benzene (Bz) to phenol (Ph) have been studied: (i) hydroxylation in the presence of an oxygen/hydrogen mixture and (ii) oxidation by molecular oxygen. The reactions were performed in a fixed-bed down-flow quartz microreactor. A 250-mg catalyst sample (fraction 0.25–0.42 mm) was mixed with double amounts (by volume) of SiC chips (0.5–0.8 mm) and loaded into the reactor. Additional SiC material was placed above the catalyst bed, to decrease the undesirable homogeneous gas-phase reactions. Oxygen/hydrogen mixtures (diluted with He) were fed into the reactor to give a total flow of $27\ cm^3/min$. The liquid, anhydrous benzene was introduced by a syringe pump, which provided a constant volume rate (0.0068 mol/h). Reaction conditions were as follows: $Bz:O_2:H_2:He = 10:5:5:80$ (mol%) and $Bz:O_2:He = 10:5:85$ (mol%); $W/F \approx 37\ g_{catal}\ h/g\,mol\,Bz$, in both cases. Before hydroxylation of benzene in the presence of an oxygen/hydrogen mixture, the catalysts were pretreated with the 5% O_2/5% H_2 mixture at 250 °C for 1 h. For the oxidation of benzene using pure oxygen, the catalysts studied were calcined at 500 °C for 1 h in a flow of O_2 (20% of O_2 in He). The conversion of benzene was studied at 250–450 °C under atmospheric pressure and steady-state conditions, which were established after 20–30 min on stream at the given temperature. The catalyst was kept for about 2 h at each measurement temperature. Reactants and products were analyzed online using a Varian 3400 gas chromatograph equipped with a thermal conductivity detector. Two columns loaded with Porapak QS and molecular sieve 13X were used for analysis.

In the aforementioned reaction, both phenol (Ph) and deep oxidation products (CO_2 and CO) were formed. For the sample with the higher Cu loading, under certain experimental conditions, we also detected (and identified using mass spectrometry) other liquid byproducts, including toluene, styrene, benzaldehyde, benzofuran, phenylpropene, acetophenone, naphthalene, biphenyl, benzophenone, fluorenone, and dibenzofuran.

Yields of the main reaction products (Ph, CO_2, and CO) and selectivity to phenol (the latter only for the 0.1Cu-ZSM-5 catalyst) reported in following section were defined as

$$Y_{Ph}\ (\text{mol\%}) = \frac{[Ph]}{[Bz]} \times 100,$$

$$Y_{CO_2}\ (\text{mol\%}) = \frac{1/6[CO_2]}{[Bz]} \times 100,$$

$$Y_{CO}\ (\text{mol\%}) = \frac{1/6[CO]}{[Bz]} \times 100, \quad \text{and}$$

$$S_{Ph}\ (\text{mol\%}) = \frac{[Ph]}{[Ph] + 1/6[CO_2] + 1/6[CO]} \times 100,$$

where Y_{Ph} is the yield of phenol (%), Y_{CO_2} is the yield of CO_2 (%), Y_{CO} is the yield of CO (%), S_{Ph} is the selectivity to phenol, [Bz] is the mol number of benzene in the feed, and [Ph], [CO_2], and [CO] are the mol numbers of phenol, CO_2, and CO produced.

In situ diffusse reflectance (DRS) UV–visible spectra were obtained using a Varian Cary 5 UV–vis-NIR spectrophotometer. The spectra were recorded in the range of 900–190 nm using both $BaSO_4$ and a PTFE (polytetrafluoroethylene) as reflectance standards. The UV–vis DR spectra are shown in Kubelka–Munk units, e.g., $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$.

Paralleling the UV–visible study, laser FT-Raman spectra of the samples were collected with a Bruker RFS100 spectrometer equipped with a diode-pumped germanium solid detector cooled with liquid nitrogen. A Nd:YAG laser was used as the excitation source ($\lambda = 1046$ nm), using a power of ca. 100 mW. Corrections concerning Rayleigh scattering (background) and white light energy were performed automatically by the Bruker software.

3. Results and discussion

Fig. 1 depicts the phenol yield obtained using our two Cu-ZSM-5 catalysts at 250–450 °C. Both samples display significant activity in the benzene to phenol transformation; in particular, the 1.0Cu-ZSM-5 sample gives a phenol yield maximum of 10.1% at 400 °C. The plot gives evidence that the phenol yield grows with the copper content of the catalyst and that the two samples studied have different thermal behaviors. Whereas the 0.1Cu-ZSM-5 catalyst shows a rising trend with temperature, the 1.0Cu-ZSM-5 sample displays an inverted U-type trend with a maximum at 400 °C. We note that the presence of H_2 in the reaction mixture has either beneficial or detrimental effects, depending on the copper loading. For the lowest copper content, a positive effect is clearly visible in Fig. 1, whereas the opposite effect occurs in the 1.0Cu-ZSM-5 catalyst. Fig. 2 shows the yield of the remaining main products detected during the reaction. As mentioned earlier, these are deep-oxidation products that are almost absent for the 0.1Cu-ZSM-5 catalyst below 350 °C and exhibit increasing values in the presence of hydrogen, except for CO_2 at 450 °C using 1.0Cu-ZSM-5. For the 1.0Cu-ZSM-5 catalyst, the products of deep oxidation behave somewhat differently with temperature compared with phenol, exhibiting no decreasing trend at high temperature. Phenol, CO_2 and CO are the only products obtained with the 0.1Cu-ZSM-5 sample. Consequently, we calculated the selectivity to phenol in this latter case and report the results in Table 2.

The joint consideration of results reported in Figs. 1 and 2 allows us to conclude that the optimal performance in the single-step transformation of benzene to phenol, the environmentally friendly reaction, is obtained with the 1.0Cu-ZSM-5 catalyst without presence H_2 at 400 °C. Note that using this catalyst, the phenol yield is approximately two times higher than reported previously [2–4,9]. These reports used different benzene to oxygen molar ratios (1:2 to ca. 1:5). However, it appears that our improved performance is associated mainly with the Cu-containing active species, because our system displays a phenol yield varying by only 1 unit (%) for benzene to oxygen molar ratios in the 2:1 (“stoichiometric” mixture, used in Figs. 1 and 2) to 1:2 (oxidant mixture) range. Above 400 °C, the presence of other organic byproducts of the reaction (listed in Section 2) allows relatively easy interpretation of the descending behavior detected for this sample (Fig. 1). Hydrogen exerts a positive influence on the phenol yield for the 0.1Cu-ZSM-5 sample (Fig. 1), improving it over the entire temperature range studied. This is not the case for the 1.0Cu-ZSM-5 sample, however, the detrimental effect reported here seems to be of moderate magnitude. A simple rationalization of the differences between our two samples with respect to the hydrogen presence in the inlet also could be due to the nature of the Cu species, as we discuss below.

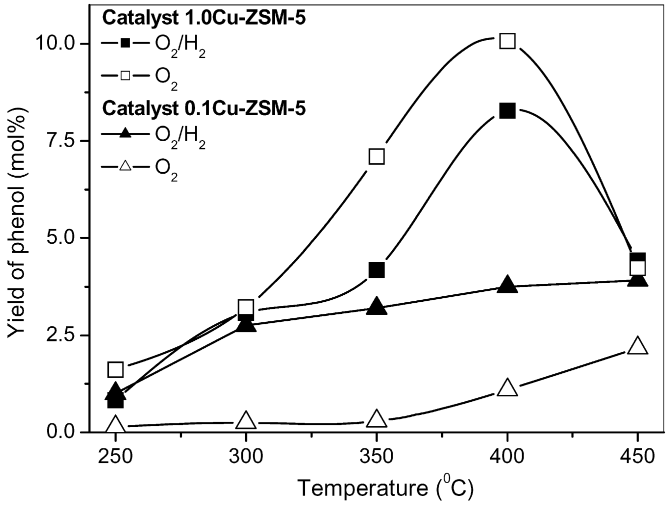

Fig. 1. Yield of phenol using the 0.1Cu- and 1.0Cu-ZSM-5 catalysts.

As an example of the catalytic system stability under reaction conditions, the oxidation of benzene to phenol was tested in two consecutive runs using both the 0.1Cu-ZSM-5 and 1.0Cu-ZSM-5 catalysts (Fig. 3). After the first run, a used catalyst was tested in the entire temperature range through the follow-

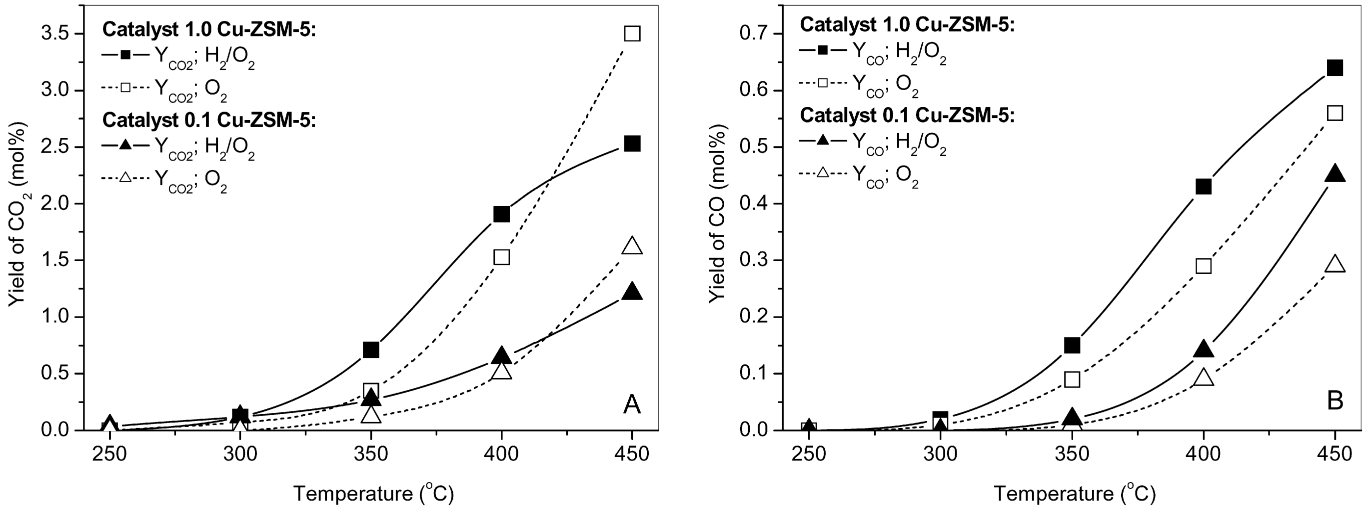

Fig. 2. Yield of the deep oxidation products: CO_2 (A) and CO (B) using the 0.1Cu-ZSM-5 and 1.0Cu-ZSM-5 catalysts.

Table 2
Selectivity and yield of phenol for the fresh and used 0.1Cu-ZSM-5 catalysts

Reaction temperature (°C)	Reaction with H_2/O_2 mixture				Reaction with molecular O_2			
	Fresh		Used		Fresh		Used	
	Y_{Ph} (mol%)	S_{Ph} (mol%)	Y_{Ph} (mol%)	S_{Ph} (mol%)	Y_{Ph} (mol%)	S_{Ph} (mol%)	Y_{Ph} (mol%)	S_{Ph} (mol%)
250	1.05	96.0	2.37	99.2	0.14	100	0.07	100
300	2.75	95.9	3.25	97.7	0.25	100	0.12	72.7
350	3.20	91.8	3.82	95.4	0.29	66.6	0.36	63.7
400	3.75	83.3	3.25	88.0	1.10	62.5	1.54	59.8
450	3.92	71.6	1.79	62.6	2.17	54.4	2.75	53.6

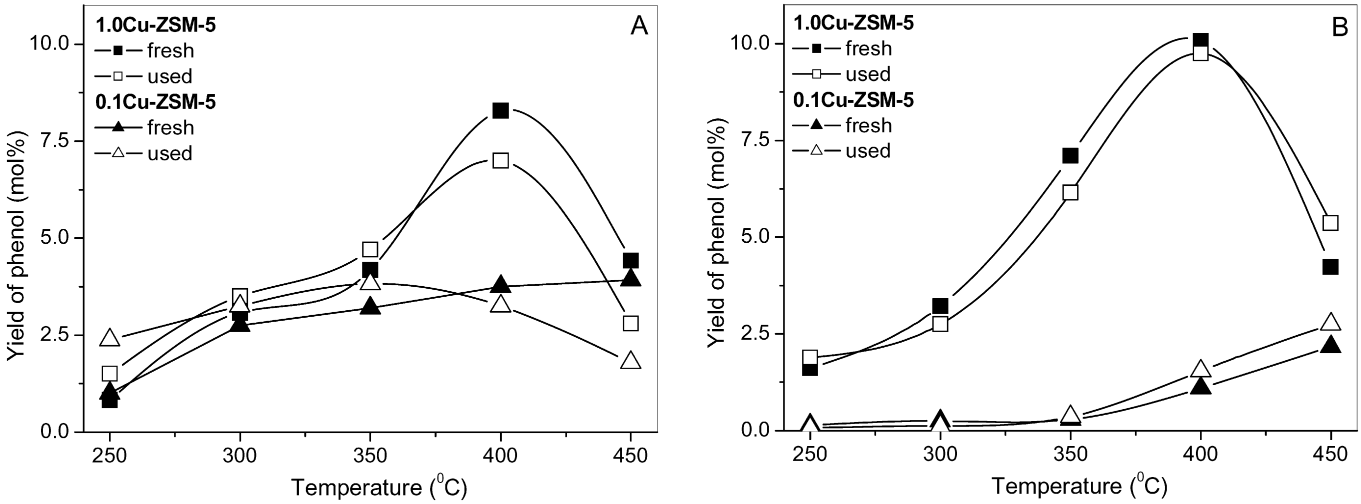

Fig. 3. Comparison between fresh and used samples in both the hydroxylation of benzene using a H_2/O_2 mixture (A) and the oxidation of Bz to Ph in the presence of O_2 (B).

ing experiment. The second catalytic test was preceded by the pretreatment detailed in the Experimental section (specific for each of the two reactions tested). In the case of benzene oxidation to phenol in the presence of oxygen, the used catalysts show no significant difference in activity compared with the fresh sample, although it give slightly higher yields of phenol at 400–450 °C. The same catalyst shows a somewhat different behavior in the hydroxylation of benzene to phenol using a H_2/O_2 mixture. Although the yield of phenol increases at temperatures below 400 °C with respect to the fresh sample, one of the catalysts (0.1Cu-ZSM-5) loses considerable activity at higher temperatures.

To provide a tentative interpretation of the catalytic activity, we characterized the solids using UV–visible (Fig. 4) and Raman (Fig. 5) spectroscopies. Enlightening results were obtained with the first technique, after dehydratation of the catalysts in N_2 at 250 °C for 1 h and then calcination in O_2 (20%)/N_2 at 500 °C for 1 h. For both samples, Fig. 4 shows the presence of isolated, octahedrally coordinated Cu^{2+} (d–d and charge transfer bands at ca. 12,000–13,000/44,000–45,000 cm^{-1}) and polymeric –Cu–O–Cu– (d–d band at ca. 16,000 cm^{-1}) species [10–12]. In the 1.0Cu-ZSM-5 sample, an additional polymeric species was also observed (ca. 17,500 cm^{-1}), which may differ from the previous one in the characteristic size. Polymeric Cu species detected in ZSM-5 give distinct UV–visible signals in correspondence with the degree of reduction (Cu(II) → Cu(I)); presumably increasing with the increasing presence of "undercoordinated" surface cations. Polymeric species containing Cu^+ ions would display lower characteristic frequencies than the fully oxidized ones [10,11]. It is interesting to stress the absence of two Cu species in both samples, the Cu–O–Cu dimers with characteristic UV–vis frequencies around 22,500 cm^{-1} [12,13] and the metallic Cu clusters (hypothetically produced in the reductive atmosphere created by decomposition of the Cu precursor during catalyst preparation), which would lead to a plasmon peak at 16,000 cm^{-1} [14]. Consequently, concerning Cu species with size potentially limited by a host effect of the zeolite, we can see that the 0.1Cu-ZSM-5 sample contains mostly isolated Cu species and a small number of polymeric Cu species, whereas the 1.0Cu-ZSM-5 sample contains these two species and additional, possibly larger polymeric clusters.

Tests made using the zeolite support only (not shown) suggest than the bands at ca. 28,500, 35,000, and 40,000 cm^{-1} displayed in Fig. 1 can be attributed mainly to the support. In other words, oxide-type Cu-containing aggregates (UV–vis band ca. 30,000 cm^{-1} [10–12]) are somewhat difficult to detect by UV–vis spectroscopy, but here they can be clearly distinguished by the presence of the signals at 297 and 347 cm^{-1} in the Raman spectrum of the 1.0Cu-ZSM-5 sample (Fig. 5). These signals are characteristic for the vibrations of the oxygen lattice atoms of the CuO structure [15,16]. CuO is detected for the 1.0Cu-ZSM-5 sample after both treatments and only after calcination (very broad peak) for the 0.1Cu-ZSM-5 catalyst. The width of the Raman peaks indicates (by phonon confinement) the small particle size of the CuO clusters present after calcination. Besides the CuO-related frequencies, Raman spectra (Fig. 5) also show broad bands (ca. 380 and 360–365 cm^{-1}) characteristic of the ZSM-5 structure and assigned to the ν_S (Si–O–Si) vibrations of the zeolite framework [17,18]. A lack of Cu(I) oxide signals is noted in the Raman spectra.

The combined in situ spectroscopic UV/Raman analysis thus indicates that the nature of the pretreatment alters the distribution of Cu among the size-limited and bulk-type species of the samples. Concerning the Cu size-limited species, it appears that calcination in O_2 at 500 °C favors dispersion of the metal, increasing the amount of isolated species and leading to the practical disappearance of the polymeric Cu species with higher nuclearity (UV band at 17,500 cm^{-1}).

Based on the foregoing characterization results, we can conclude that the contact-induced ion-exchange procedure used here limits the presence of isolated or quasi-atomically dispersed (dimers, trimers) species in the resulting copper-containing solids and leads to the production of polymeric-type aggregates of limited size. This seems to be a direct consequence of the solid-state preparation method used, which may lead to small clusters of Cu after decomposition of the pre-

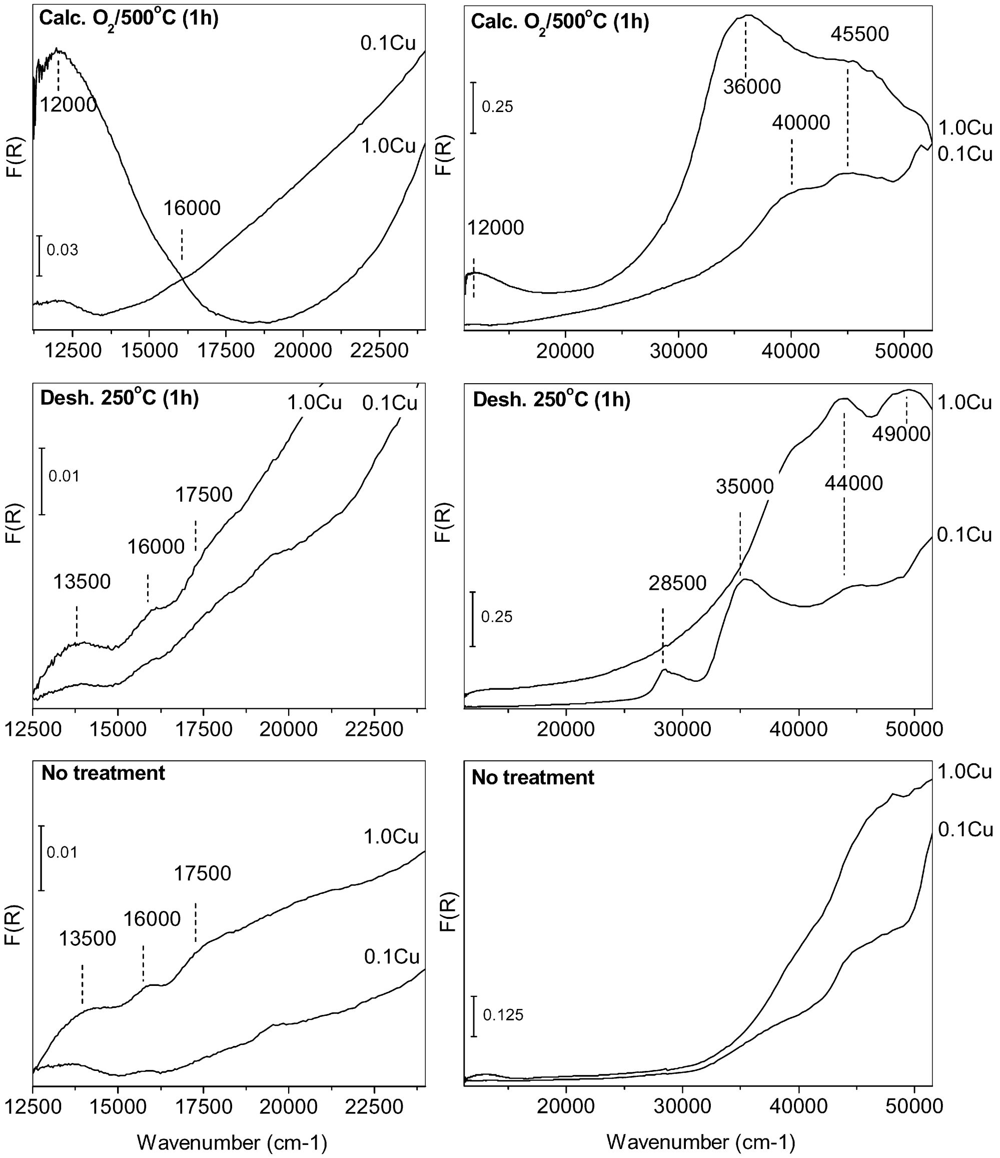

Fig. 4. UV–Vis spectra for the 0.1Cu-ZSM-5 and 1.0Cu-ZSM-catalysts. UV spectra were recorded at room temperature for the initial samples, after 1 h dehydratation at 250 °C, and after calcinacion at 500 °C in O_2(20%)/N_2.

cursor (240 °C) and also may limit the presence of isolated Cu species at cationic positions of the zeolite (typical of the liquid-phase preparation methods). Growth of the polymeric-type species with the copper content of the material is therefore observed (Fig. 4), suggesting that the production of phenol as a partial oxidation product is maximized in the presence of such copper-polymeric species. Note however, than the increasing presence of isolated-type copper species (cations, dimers) in the 1.0Cu ZSM-5 sample after calcination indicates that these Cu-containing species also catalyze the benzene-to-phenol transformation. Such isolated species have been previously described as the active centers of the selective oxidation [4,9]. Thus, although the production of phenol is clearly related to size-limited Cu species, the relative reaction rate of isolated and polymeric species is unknown, and here we can only confirm that both types of species are present in the most active samples. On the other hand, the presence of bulk oxide entities (mainly in the 1.0Cu-ZSM-5 catalyst) may be linked to formation of the organic byproducts mentioned in Section 2, which were obtained exclusively on the catalyst with the higher Cu content. Finally, it can be mentioned that the observed differences in O_2 versus O_2/H_2 are possibly connected with the higher dispersion of the Cu active species reached after calcination in pure oxygen. Potential differences in the competition of benzene and hydrogen oxidations and/or effects due to water in the absorption of reactants could be the origin of this finding [8].

4. Conclusions

This study provides evidence that the copper form of the ZSM-5-type zeolite obtained by contact-induced ion exchange is very active for formation of phenol in the catalytic, gas-phase oxidation of benzene using O_2 and H_2/O_2. These two gas mix-

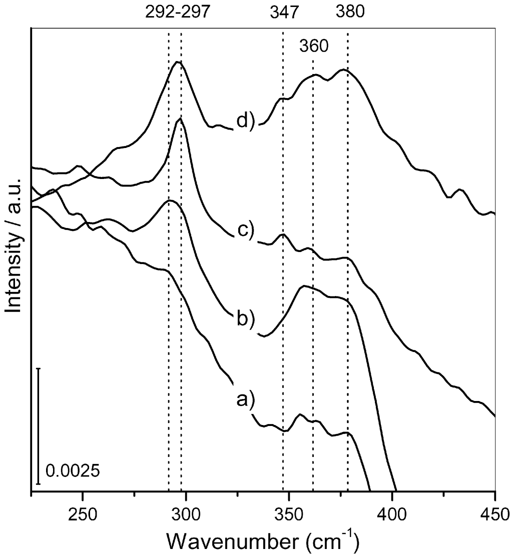

Fig. 5. Raman spectra for the 0.1Cu-ZSM-5 (a, b) and 1.0Cu-ZSM-5 (c, d) catalysts: after 1 h dehydratation at 250 °C (a, c) and after calcinacion at 500 °C in O_2(20%)/N_2 (b, d).

tures could have significant advantages over the environmental unfriendly and dangerous N_2O oxidant used in Fe-ZSM-5 systems [5–7]. The catalyst preparation procedure allowed us to obtain phenol as the main organic product in the abovementioned reaction, whereas the presence of hydrogen in the feed gave rise to either beneficial or detrimental effects, depending on the Cu loading in zeolite.

For both catalysts studied, the phenol yield increased with temperature. For the sample with a 10% of Cu, the phenol yield increased monotonically to give a maximum of 4.2 % at 450 °C in the presence of O_2/H_2 mixtures, whereas for the catalyst with 100% Cu, the yield of phenol rose sharply to reach a relatively high value of ca. 10% at 400 °C in the exclusive presence of O_2. For this catalyst, a further increase in temperature caused a decreased phenol yield with the concomitant presence of additional organic products. No significant differences between the used and fresh catalysts were found.

Characterization of the Cu systems suggests that an optimum phenol yield can be associated with the presence of size-limited (isolated and/or polymeric) Cu species. This provides key information for improving results in future studies. Finally, the size/reducibility of such species might be a key factor governing the selectivity of a catalyst, particularly when using the O_2/H_2 mixture.

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