The role of carriers in properties and performance of Pt-CuO nanocatalysts in low temperature oxidation of CO and p-xylene

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Abstract
In this study four optimal catalysts on the basis of Pt–CuO supported on γ-Al₂O₃, TiO₂, CeO₂ and γ-Al₂O₃+CeO₂ have been prepared and studied. Characterizations of the catalysts have been carried out by methods of N₂ adsorption, x-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and temperature-programmed-reduction (TPR). The activity of these catalysts for deep oxidation of CO, p-xylene and their mixture was assessed at temperature range 75–300 °C. The results showed that the presence of CO in a mixture with p-xylene has a beneficial effect on the rate of p-xylene conversion; meanwhile the presence of p-xylene shows the inhibition on CO oxidation. In the reactions of the mixture, oxidation of CO and p-xylene occurred simultaneously on PtCuO catalyst supported on γ-Al₂O₃, TiO₂, CeO₂ carriers, but on catalyst PtCu/CeAl the oxidation of p-xylene can proceed only when CO is consumed entirely. Addition of 1.1 to 3.2% mol steam into the gas mixture exhibits no effect on the conversion of CO; meanwhile, it shows the limited effect on oxidation rate of p-xylene on hydrophobic catalysts (PtCu/Ce, PtCu/CeAl and PtCu/Ti), but strong inhibition on hydrophilic catalyst (PtCu/Al). However, this negative effect of water was reversible.

Keywords: low temperature deep oxidation, Pt-CuO, CO, p-xylene, carriers

Mathematics Subject Classification: 5.06

1. Introduction
Catalytic oxidation is considered as one of the effective and economical ways of removal of impurities in industrial gases emission to meet environmental standards. Carbon monoxide and aromatic hydrocarbons such as xylene are prominent environmental pollutants, therefore, to look for effective catalysts, enabling one to oxidize CO and volatile organic compound (VOC) at low temperatures, is an important task for researchers in the fields of chemistry and chemical technology. The advantage of low temperature oxidation is to reduce fuel consumption for conversion of large volumes of polluted air.

In general, precious metal catalyst is more advantageous for purification of mixtures of gases containing aromatic compounds and does not contain catalyst poisons (such as sulfur compounds), thanks to the reaction requiring lower temperatures [1]. Metal oxides are an alternative to noble metals as catalysts for total oxidation. For some applications, the higher overall loading of metal oxides in the catalysts makes them more resistant to poisoning than noble metals, while precious metal catalysts with a limited number of active sites could be quickly poisoned by small quantities of poisons [2]. Promotion of Al, Cr, Cu, Mn and Co catalysts by Pt has improved their activity for CO oxidation and resistance to SO₂ poisoning [3]. The highest activity in oxidation of CuO/
CeO₂ catalysts modified with Pt, is explained by the strong link between the Pt with CuO/CeO₂. Meanwhile, modification of CuO/CeO₂ catalysts by Pd or Rh led to reduced catalysts activity in selective oxidation of CO, due to high activity of additives in the oxidation of H₂ [4]. Meanwhile, the role of metal oxides is to diminish the CO inhibition, which is a typical characteristic of reaction at low temperatures on platinum catalysts [5].

Thanks to outstanding properties such as high porosity and large specific surface, fairly uniform structure and high thermostable, γ-Al₂O₃ is widely used as a carrier for the catalyst. In our previous studies [6–9] the optimal compositions of metal oxide catalysts for complete oxidation of CO and p-xylene have been determined as follows: 10 wt.% CuO/γ-Al₂O₃, 7.5 wt.% CuO/γ-Al₂O₃, 12.5 w.% CuO/γ-Al₂O₃ (P25Degusa), and 10 wt.% CeO₂/20 wt.% CeO₂ + γ-Al₂O₃ (Cu/γ-Al₂O₃). These samples have been found to be the most active and stable for the complete oxidation of CO, p-xylene and their mixture. In the study [10], the optimal concentration of Pt for catalysts mentioned above of 0.1 wt.% has been determined.

As follows from previous investigation, the CO oxidation over the CuO/Al₂O₃, CuCr/Al₂O₃ [6] and Pt/Al₂O₃ [11] catalysts at low temperature was inhibited by steam. This may be due to the hydrophilic property of alumina. Reasonably, hydrophobic catalysts can avoid this problem. Furthermore, as is known, organic compounds are better adsorbed on a hydrophobic surface than on a hydrophilic one. Therefore, hydrophobic carriers such as CeO₂ and TiO₂ are also studied to be used for mixed catalysts in the low temperature oxidation of CO and VOC in this investigation.

2. Experimental

In the study, 4 following catalysts with the optimal composition: 0.1 w% Pt + 10 wt.% CuO/γ-Al₂O₃ (PtCu/Al), 0.1 w% Pt + 10 wt.% CuO/γ-Al₂O₃ (PtCu/Al), 0.1 wt.% Pt + 7.5 wt.% CeO₂/γ-Al₂O₃ (PtCu/Ce), and 0.1 wt.% Pt + 12.5 wt.% CeO₂/γ-Al₂O₃ (PtCu/CeAl) were synthesized by sequential impregnations followed by the procedure described in our previous work [10]: firstly with an aqueous solution of Cu(NO₃)₂.3H₂O, Ce(NO₃)₃.6H₂O, H₂PtCl₆ complex and urea in a minimum volume of de-ionized water. After drying in room temperature for 24 h, at 80 °C for 2 h and at 110 °C for 2 h, all the samples were treated at 600 °C for 4 h in an air flow.

Brunauer–Emmett–Teller (BET) specific surface area of the obtained catalysts was determined from N₂ adsorption isotherms at 77 K on a Quantachrome NovaWin machine. Phase composition of catalysts was characterized by x-ray diffraction (XRD) method on the apparatus, Shimadzu x-ray diffractometer XD-5A. Characteristics of reduction were investigated by method of temperature-programmed-reduction (TPR) on the apparatus, Chembent 3000, as described in [7]. The morphology of the synthesized catalysts was obtained using field emission scanning electron microscopy (SEM, JEOL 7401) and transmission electron microscopy (TEM, JEOL 1400).

Before running the reaction, the catalysts were activated for 2 h at 300 °C in an air flow with velocity of 12 L h⁻¹. Activity of the catalysts in deep oxidation of CO, p-xylene and their mixture was studied in a microflow reactor at the temperature range 75–300 °C, concentrations of O₂, CO and p-xylene in the stream were 10.5, 0.5 and 0.34 mol%, respectively, volume velocity of stream was 12 L h⁻¹, catalyst weight was 0.2 g. Reaction mixtures were analyzed on a gas chromatograph of agilent technologies 6890 plus with a thermal conductivity detector (TCD), capillary column HP-PLOT MoleSieve 5A (30 m length, 0.32 mm outer diameter, 0.25 μm thickness) and an FID detector, capillary column DB 624 (30 m length, 0.32 mm outer diameter, 0.25 μm thickness).

3. Results and discussion

3.1. Physico-chemical characteristics of catalysts

From the field emission scanning electron microscopy (FE-SEM) image (figure 1) it follows that, there are the particles of catalyst in the form of the ball shape existed on the surface of catalysts. On TEM images (figure 2) the dispersed particles Pt in size of 1–3 nm and CuO clusters with dimension of a few tens nm on surface of the catalysts could be observed. Crystal size of CuO calculated by XRD pattern (figure 3) at the angle 2θ = 35° of PtCu/Al and PtCu/Ti was determined to be 18.8 and 26.2 nm, respectively. The agglomeration of CuO particles into large clusters, as observed in TEM image (figure 2), covering the surface of carriers led to significant reduction in the specific surface area of catalyst. The specific surface area of the carriers of 252, 103 and 45 m² g⁻¹, corresponding to γ-Al₂O₃, CeO₂, and TiO₂-P25 were determined, while these values for PtCu/Al, PtCu/CeAl, PtCu/Ce, PtCu/Ti catalysts are 95.9, 80.1, 14.8, and 16.2 m² g⁻¹, respectively. Besides, for PtCu/Ti catalyst, after heat treatment at 600 °C, content of the rutile phase in TiO₂, calculated according to the intensity of characteristic peak of rutile phase at the angle 2θ = 27.5° by formula shown in [14], was 93.8%, so TiO₂ in the form of large spherical particles (approximately
50–100 nm) can be observed in figure 2(d). It is the second reason leading to low specific surface area of the catalyst PtCu/Ti.

As seen from figure 2, dimension of Pt particles and CuO clusters on PtCu/Ce is smallest and on PtCu/Ti is biggest. On PtCu/Ce sample the values of agglomerates size of Pt and...
CuO are 1 nm and 10 nm, respectively, while on PtCu/Ti these values are 1–3 nm and 40–60 nm, respectively.

As seen on XRD pattern of PtCu/Al catalyst (figure 3, line 1) the CuO phase is characterized by the most intensive peaks, the characteristic peaks of γ-Al2O3 and of aluminate CuAl2O4 are very weak; at the same time the characteristic peaks of Pt with low intensity can be observed. XRD pattern (line 3) of catalyst PtCu/Ce is quite similar to that of PtCu/CeAl (line 2), characterized by intensive characteristic peaks of the cubic fluorite structured CeO2 at 2θ = 28.6°, 33°, 47.4°, 56.3°, 59°, 69.4°, 76.7°, 79° [15] and very weak peaks, characteristic of CuO, γ-Al2O3, and Pt. However, the intensity of characteristic peaks of CeO2 in PtCu/CeAl catalyst has been observed to be significantly weaker compared to those in the PtCu/Ce sample. It indicated that the interaction of CeO2 with Al2O3 made cerium oxide to be crystallized in smaller agglomerate. Additionally, the TPR profiles in figure 4 are consistent with these observations because the reduction peak around 687 °C for the PtCu/Ce catalyst, which has been assigned to bulk CeO2, is absent in the profile of the PtCu/CeAl catalyst. Furthermore, the XRD patterns of the two samples containing CeO2 (PtCu/CeAl and PtCu/Ce) showed very weak CuO reflections, indicating that the copper oxide phase exists in a highly divided or amorphous state on the surface of ceria, or the formation of solid solution, or a combination of these two phenomena [12]. XRD results of the catalysts PtCu/Ti (figure 3, line 4) showed the intensive characteristic peaks of TiO2 in rutile phase (2θ = 27.5°, 36.1°, and 54.3°) and characteristic peaks of CuO and Pt with low intensity.

XRD analysis results showed that γ-Al2O3 exists in the catalysts in the amorphous state, and that on TEM image (figure 2(a)) of PtCu/Al very small porous particles of Al2O3 can be observed. CeO2 in PtCu/Ce and PtCu/CeAl samples exists in the crystalline state with the crystallite size of 11.8 nm and 7.1 nm, respectively. The crystallite size of TiO2 in PtCu/Ti sample of 34.5 nm was determined. The order in the intensity of the characteristic peaks of CuO and CuO crystallite size in the catalyst Pt–CuO supported on various carriers was observed as follows: Al2O3 > TiO2 > (CeO2 + Al2O3) ≈ CeO2. This indicates that CuO dispersed on CeO2 better than on Al2O3 and TiO2.

In a TPR diagram of the PtCu/Al sample (figure 4, line 1), a peak at T_{max} = 274 °C and a shoulder at about 400 °C can be observed. Dow et al [16] reported that for the CuO/Al2O3 catalyst, a peak with a maximum at 210 °C is created due to the reduction of the highly dispersed copper oxide species and the reduction peak with T_{max} > 250 °C has been ascribed to the reduction of bulk-like CuO phases. In our previous paper [17] the TPR profile of Cu/Al sample is characterized by two main reduction peaks: a peak at T_{max} = 375 °C was attributed to the reduction of buck CuO phase and another peak with lower intensity at T_{max} = 300 °C of small cluster CuO. According to Lenarda et al [18], CuO buck shows one reduction peak at 400 °C due to complete reduction of Cu2+ to Cu°. Subramanian [19] reported that the hydrogen reduction process of Pt/Al2O3 system takes place at the temperature range of 300 –500 °C, but Castro et al [20] points out that on TPR diagram of Pt/Al2O3, a reduction peak at 240 °C due to reduction of platinum can be observed. Therefore, it can be suggested that the peak at T_{max} = 274 °C in the TPR diagram of the PtCu/Al sample characterizes the reduction of small cluster CuO and a
shoulder at about 400 °C characterizes the reduction of non-associated buck CuO on the surface of catalyst.

The TPR diagram of catalyst PtCu/CeAl shows only one peak at 255 °C, which is assigned to the reduction of small clusters CuO. Our group previously reported that there were two reduction peaks in Cu/CeAl catalyst: the peaks in the range of 215–245 °C are attributed to the reduction of small clusters copper oxide and of larger CuO particles, respectively [8]. In the case of this study, the appearance of only one reduction peak at lower temperature (255 °C) on TPR profile of PtCu/CeAl can be explained by the formation of small CuO particles on the surface of alumina when catalyst was promoted by a small amount of Pt. The maximum reduction temperature of CuO on the Pt-promoted (PtCu/Al and PtCu/CeAl) markedly lower than that on the non-promoted sample Cu/Al, suggesting that the redox properties of CuO and the morphologies of catalysts are significantly affected by Pt as well as CeO2. Furthermore, it can be observed from table 1 that the reduction extent of CuO increases from 36.7 to 45.8% when the Al2O3 support is modified with ceria addition.

The TPR diagram (figure 4, line 3) for the PtCu/Ce catalyst shows a main reduction peak at 214 °C, two small peaks at 545 °C and 687 °C and a small shoulder at about 184 °C. Avgoustopoulos et al [12] observed three reduction peaks in the TPR profiles of CuO–CeO2 catalysts prepared by the urea-nitrates combustion methods; one at about 170 °C attributed to the reduction of highly dispersed copper oxide strongly interacting with the ceria surface, and the peaks at higher temperature (about 220 °C and 255 °C) attributed to the reduction of larger CuO particles less associated with ceria. According to Wu et al [21] a peak at about 800 °C in the TPR profile of Cu1Ce4 is attributed to the reduction of bulk oxygen atoms in CeO2. In another publication [22], Wu reported that there were four overlapping reduction peaks presented in CuO–CeO2 catalyst: the peaks in the range of 134–140 °C and 183–204 °C were attributed to the reduction of noncrystalline CuO strongly interacting with CeO2 and of larger CuO particles less associated with CeO2, respectively. The peaks in the range of 215–219 °C and 248 °C represented the reduction of bulk copper oxide associated with CeO2 to some extent and the reduction of pure bulk copper oxide, respectively. Therefore, it can be suggested that the peak at 214 °C on TPR diagram of the PtCu/Ce sample (figure 4, line 3) characterizes the reduction of small buck copper oxide associated with CeO2, the peaks appearing at higher temperature (about 545 and 687 °C) are most probably due to the reduction of Pt particles associated with ceria and of CeO2, respectively [18]. The small shoulder at about 184 °C is attributed to the reduction of highly dispersed copper oxide strongly interacting with the ceria surface. For the PtCu/Ti sample (curve 4 in figure 4) an intense peak at 233 °C and two small ones, less defined, at about 275 and 415 °C can be seen. It can be suggested that the peaks at Tmax = 233 °C and 275 °C were attributed to the reduction of small clusters of copper oxide strongly interacting with TiO2 and of bulk CuO weakly associated with TiO2, respectively. The peak appearing at 415 °C are probably due to the reduction of pure bulk copper oxide.

### 3.2. Catalytic performance for deep oxidation

Results of catalytic performance tests obtained over various Pt–CuO catalysts are summarized in figure 5, where conversion of CO, p-xylene individually and in the mixture (Xi) is plotted as a function of reaction temperature. It should be noted that the only product detected in these experiments is CO2. The ’light-off’ temperatures for 50% (T50) and 100% (T100) conversion of CO and p-xylene individually and in the mixture of the catalysts are shown in table 2.

Conversion of CO and p-xylene increases with increasing temperature and the conversion curves in all cases and on all catalysts are similar to each other. Furthermore, the light-off curves were steep for all catalysts except for CO oxidation on PtCu/Al sample (figure 5). Compared to oxidation of single p-xylene, in the case of oxidation of single CO, all catalysts express higher activity. It has been shown in table 2 that the light-off temperatures (at about 50% conversion) of CO is lower than that for p-xylene from 90 to 170 °C. Complete conversion of p-xylene on all catalysts is reached at 300 °C and the complete oxidation of CO is achieved at around 125–275 °C. Thus, from the obtained results in table 2 it is possible to order the catalysts on the basis of their activities (temperatures of 50%- and 100%-conversion of carbon monoxide and p-xylene) as follows: PtCu/CeAl ≈ PtCu/Ce > PtCu/Ti > PtCu/Al.

Compared to Cu/Al catalyst (not shown), addition of 0.1 wt.% Pt, the temperature for 50%-conversion of CO reduced from 225 °C down to 165 °C, and the temperature for 100%-conversion of CO reduced from 300 °C down to 275 °C. The positive effect of platinum can be explained as follows: by weakening the interaction Cu–Al2O3 the added Pt

### Table 1. Characteristics of the obtained catalysts. The values of surface specific area (S BET), crystal size of TiO2 rutile phase at the angle 2θ = 27.5°, CeO2 at 2θ = 28.6° (d XRD(CeO2) and CuO at 2θ = 35° (d XRD(CuO), and maximum reduction temperature (T max), extent of reduction (K red)).

| Catalysts      | CuO content (%) | S BET (m² g⁻¹) | d XRD(CeO2) (nm) | d XRD(CuO) (nm) | T max (°C) | K red (%) |
|----------------|-----------------|---------------|-----------------|----------------|------------|----------|
| PtCu/Al        | 10              | 95.9          | —               | 18.8           | 274; 400   | 36.7     |
| PtCu/CeAl      | 10              | 80.1          | 7.1 (CeO2) n.d  | 255            | 45.8       |
| PtCu/Ce        | 7.5             | 14.8          | 11.8 (CeO2) n.d | 184; 214; 545; 687 | 32.2       |
| PtCu/Ti        | 12.5            | 16.2          | 34.5 (TiO2-R)   | 233            | 17.2       |
enables it to enhance the reducibility of catalyst (the extent of reduction of CuO increased from 13 to 36.7% and maximum reduction temperature decreased from 300 to 274 °C).

It is observed that two catalysts containing CeO2 (PtCu/CeAl and PtCu/Ce) are the most active catalysts of this series, exhibiting measurable conversion of CO at temperatures as low as 75 °C and reaching 100% CO conversion at around 125 °C. It was found that CeO2 depressed the formation of massive CuO, on these catalysts the copper oxide phase exists in a highly divided or amorphous state, as indicated the XRD pattern, reducing at low temperature. PtCu/CeAl is the only catalyst, in which CuO exists only in the form of highly dispersed CuO with the highest degree of reduction of this series of catalysts. PtCu/Ce is the only the catalyst; in its TPR diagram the reduction peak of Pt (T\text{max} = 545 °C) was observed. From the EDS and EDX data (figure 6), it follows that Cu and Pt are evenly distributed on the surface of CeO2 of the PtCu/Ce catalyst, and Pt content on the catalyst surface reaches 10.14 wt.%, significantly higher than the Pt content of catalyst (0.1 wt.%), suggesting a strong concentration of Pt on the catalyst surface, that should lead to the appearance of the reduction peak of ion Pt on TPR diagram.

As follows from table 2, among the studied catalysts, PtCu/Al exhibited the worse activity for combustion of CO, p-xylene as well as for their mixture, compared to the rest. It may relate to the contribution of bulk CuO and the maximum reduction temperature of CuO on PtCu/Al being highest. Luo et al [23] previously reported that the finely dispersed CuO is responsible for the high catalytic activity for low-temperature CO oxidation, while the bulk CuO contributes little to the activity.

It follows from the presented results in table 2 that the catalysts containing CeO2 (PtCu/CeAl and PtCu/Ce) expressed very high activity in CO oxidation; the entire oxidation of CO could be reached at a very low temperature (125 °C), 150 degrees lower than that for the catalyst without CeO2.

![Figure 5. The light-off curves of CO and p-xylene individually (dashed line) and in the mixture (full lines) (X) for studied Pt–CuO catalysts: (a) PtCu/Al, (b) PtCu/CeAl, (c) PtCu/Ce and (d) PtCu/Ti.](image)

### Table 2. Light-off temperatures for catalysts in oxidation of substances individually (I) and in the mixture (II).

| Catalysts | \(T^\text{CO}_{50}\) (°C) | \(T^\text{CO}_{100}\) (°C) | \(T^\text{xyl}_{50}\) (°C) | \(T^\text{xyl}_{100}\) (°C) |
|-----------|----------------|----------------|----------------|----------------|
| PtCu/Al   | 165            | 275            | 262            | 300            |
| PtCu/CeAl | 89             | 125            | 187            | 200            |
| PtCu/Ce   | 85             | 125            | 212            | 225            |
| PtCu/Ti   | 140            | 200            | 262            | 275            |

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(PtCu/Al). However, for p-xylene oxidation, CeO$_2$ did not express its effect clearly. Also, the results obtained by authors [24] indicated that CeO$_2$ played a promoting role in CO oxidation but displayed very little influence in oxidation of methane, ethanol and ethyl acetate.

As can be observed from figure 5, in the presence of p-xylene the conversion of CO is retarded, catalysts become active for CO oxidation at temperatures of 150–200 °C, significantly higher than in the case of oxidation of single CO. Figure 5 shows remarkable shift of the conversion curve of CO towards the higher temperature region; meanwhile, for the conversion curve of p-xylene a shift in the opposite direction, a lower temperature region with different rates, in comparison with the oxidation of individual components. In the mixture with p-xylene, temperature of 50% CO conversion is around 187–262 °C (table 2), about 97–127 °C higher than that in case of oxidation of single CO. Meanwhile, in the mixture value of temperature of 50% conversion of p-xylene remained nearly unchanged on PtCu/Al and about 18–46 °C lower than in the case of oxidation of individual p-xylene.

Thus, one can notice the identical mutual influence of CO and p-xylene on each other in oxidation of their mixtures on the catalyst based on Pt-CuO, but this observation is considerably different from that on noble metals (Pt, Pd and Rh) catalysts [25]. The increase of temperature of hydrocarbons oxidation in the mixture with CO compared to absence of CO to achieve the same conversion is a fairly common phenomenon for noble metal catalysts [25]. On Pt surfaces, CO adsorbed stronger than hydrocarbons and occupied almost the whole surface of Pt, so it expressed inhibition on the oxidation of hydrocarbons [26]. Also, due to the influence of the adsorption of hydrocarbons the temperature of CO oxidation in the mixture to achieve the same conversion is higher than that in the case of CO individually. In this study, the shift of the conversion curve of p-xylene towards the lower temperature region can be explained by two reasons. The first reason is the presence of a large amount of CuO centered on the surface of catalysts, which should be able to increase the adsorption of p-xylene, and the second reason is the additional heat generation from CO oxidation or the formation of specific intermediates in the conversion of the additive substance [27]. It has been found from study of catalytic combustion of chlorobenzene on a 2 wt.% Pt/γ-Al$_2$O$_3$ catalyst in binary mixtures with various hydrocarbons (toluene, benzene, cyclohexane, cyclohexene, 1, 4-cyclohexadiene, 2-butene, and ethene) and with carbon monoxide in [28] that, compared to single substances oxidation, the reaction rate of combustion of substances in a binary mixture can increased or decreased.

As can be observed from figure 5, in the oxidation of mixture on the PtCu/Al, PtCu/Ce and PtCu/Ti the conversion curve of CO and p-xylene is almost identical, suggesting that processes of CO and p-xylene oxidation proceeded practically simultaneously and the temperature of 100% conversion of CO and p-xylene is approximately the same. This result indicates identical adsorption properties of these reactants on these catalysts and/or the common intermediate containing both CO and p-xylene, was formed. Meanwhile, on PtCu/CeAl, one can observe the p-xylene conversion reached only 44% when CO was almost completely converted. It is possible to propose a preference on catalysts PtCu/CeAl for CO adsorption over xylene adsorption on the surface of the catalyst. In this case, xylene can be adsorbed and oxidized to a considerable extent only after the surface has been released from CO [25]. Nevertheless, the competitive adsorption of p-xylene, in different extents on different catalysts, could increase the temperature of 50% conversion ($T_{50}$) of CO.

3.3. The effect of water on stability of the catalysts

As previously reported, moisture dramatically influences VOC oxidation in most cases, especially at low temperatures. Figure 7 shows the life test of catalysts in reaction in dry and humid medium. The total oxidation of CO and p-xylene over studied catalysts was carried out continuously in dry condition for more than 30 h. As can be seen from figure 7, the conversion remains constant at $\sim$85% for the 30 h of the test. This leads us to believe that these samples have a high stability.

When steam (from 1.1 to 3.2% mol) was added at 180 °C to the gas stream, the oxidation of CO on all catalysts was stable and the concentration of water in the gas mixture had no effect on the conversion of CO (figure 7(a)). Meanwhile, adding of steam showed the different effect on activity of various catalysts for the oxidation of p-xylene into CO$_2$ at 267 °C. On two catalysts, containing CeO$_2$ (PtCu/CeAl and PtCu/Ce) the limited effect of water on oxidation rate was obtained (figure 7(b)). The oxidation of xylene into CO$_2$ over
PtCu/Ti was slightly reduced from 85\% to about 65\% (figure 7(b)) when concentration of water in the gas mixture increased from 1.1 to 3.2\% mol. This low effect of water can be explained by the presence of hydrophobic supports. In the case of PtCu/Al, catalyst prepared from a hydrophilic support $\gamma$-Al$_2$O$_3$, xylene oxidation at 267 °C was strongly inhibited by the presence of water (figure 7(b)). The conversion of p-xylene into CO$_2$ passed from 85\% to 5\% when the water was added to the feed, and the higher the concentration of steam added, the stronger the inhibition that was observed. However, this negative effect of water was reversible, which suggests that metallic sites were not modified by the presence of steam. The strong influence of steam on oxidation of p-xylene without effect on the conversion of CO on hydrophilic catalyst PtCu/Al can be explained by the preferred adsorption of CO on Pt surface, but p-xylene on metal oxide surfaces.

The diversity of effect of steam on oxidative activity of precious metal catalysts was also mentioned by other authors [29–32]. Commonly, the effect of steam depends on the nature of reactant and of catalyst. Thus, during oxidation of chlorinated compounds, the presence of steam retards the conversion on Pd catalysts, while on Pt the activity is enhanced [29]. Moreover, CO oxidation can be significantly inhibited by the presence of water in feed stream [30]. According to Patrick Magnoux et al [31], the hydrophobicity of the support might offer advantage for the oxidation of various VOC in the presence of moisture. The results in [32] indicate that activity of Pt/activated carbon for complete oxidation of BTX is only slightly influenced by moisture because of negligible water adsorption or condensation of activated carbon.

4. Conclusion

In conclusion, the catalyst contained CeO$_2$ (PtCu/Ce and PtCu/CeAl) expressed the best activity in oxidation of CO, p-xylene as well as their mixture. This catalyst is able to oxidize completely CO and p-xylene individually at 125 °C and 300 °C, respectively, and make the same for these reactants in their mixtures at 200−225 °C and 225−275 °C, respectively.

The presence of CO in a mixture with p-xylene has a beneficial effect on the rate of p-xylene conversion, meanwhile presence of p-xylene shows the inhibition on CO oxidation. The temperature for 50\% CO conversion has increased from 97 to 127 °C, and the temperature for 50\% p-xylene conversion decreased from 5 to 46 °C.

On PtCu/Al, PtCu/Ce, PtCu/Ti catalysts the processes of oxidation of both the reactants could proceed simultaneously, meanwhile, on PtCu/CeAl catalyst oxidation of p-xylene can proceed only when CO is consumed entirely; nevertheless, the p-xylene adsorption also can reduce the intensity of CO oxidation.

Addition of steam into the gas mixture has no effect on the conversion of CO; meanwhile, it shows limited effect on oxidation rate of p-xylene on hydrophobic catalysts (PtCu/Ce, CeAl).
PtCu/CeAl and PtCu/Ti), but strong inhibition on hydrophilic catalyst (PtCu/Al). However, this negative effect of water was reversible. Hence, PtCu/Ce and PtCu/CeAl showed themselves to be the most active and stable catalysts for deep oxidation of CO, p-xylene and their mixture in humid gas.

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