Acetone transformation over PtCu/H[Al]ZSM5 catalysts. Effect of copper content

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Received 8 December 2000; accepted 19 September 2001

A series of bifunctional bimetallic PtCu/H[Al]ZSM5-type catalysts was prepared and acetone transformation was carried out over them at 160 °C, 1 atm, acetone/hydrogen molar ratio $= 3$, and WHSV (weight of reactant injected per weight of catalyst per hour) ranging between 9.4 and 38 h^{-1}. According to the results, as copper atomic fraction ($X(\mathrm{Cu})$) increases in the bimetallic catalyst, propane formation rate decreases and methyl isobutyl ketone (MIBK) formation rate increases until $X(\mathrm{Cu})$ equals 0.40. These results suggest that active metallic centers for the olefin double bond hydrogenation in the α-β unsaturated ketone, which leads to the MIBK formation, do not appear to be those hydrogenating the acetone carbonyl double bond to form propane. When $X(\mathrm{Cu}) > 0.40$, MIBK formation rate considerably decreases, meaning that practically all platinum metallic centers have been passivated for those copper atomic fractions over the PtCu/H[Al]ZSM5-type catalyst. Therefore, catalysts begin to act only by means of the acid function, and as a result a logical increase in the mesityl oxide (MO) concentration occurs, a substance that is formed by means of an acid catalysis.

KEY WORDS: acetone; methyl isobutyl ketone; platinum–copper; HZSM5; bifunctional monometallic and bimetallic catalysts

1. Introduction

4-methyl-2-pentanone, commonly known as methyl isobutyl ketone (MIBK), one of the most popular ketones worldwide, is an asymmetric ketone widely used in the manufacturing of paints, lacquer and varnishes, as well as a solvent for nitrocellulose, ethyl cellulose and natural and synthetic resins [1,2]. It is industrially obtained from acetone by means of a rather unpractical process consisting of three stages (aldolization–dehydration–hydrogenation) [3]. The first two stages require acid or basic catalysis, which implies the use of high pollutant substances [4]. However, a new methodology has been lately used to study this process, which begins with acetone and hydrogen and uses bifunctional catalysts of the noble metal type, supported over acid or basic solids. In this sense, catalysts such as Ni/Al_2O_3 [5], Pd/MgO [6], Pd/H[Al]ZSM5 [7,8], and Pt/H[Al]ZSM5 [9] have been used.

This new procedure is much more interesting, because it includes neither mineral acids nor bases (highly corrosive reagents) apart from the fact that the product and the catalyst can be more easily separated. However, in these cases the solid used as a support should have very specific characteristics, even more if the purpose is to prepare MIBK selectively, because amorphous solids, both acid as well as basic, pose serious problems regarding product selectivity due to the changing size of their cavities and pores. This leads to the formation and diffusion of a large number of substances with high molecular weight and volume, such as isophorone and isoxylitones [10], and this, in turn, results in lower selectivity in the formation of the MIBK product. On the other hand, crystalline aluminosilicates, such as HY, HMOR, and HZSM5 zeolites, are solids with regular-size cavities and pores; however HZSM5 has been found to have cavities and pores with the proper size to synthesize 4-methyl-3-penten-2-one (MO), the closest intermediate to MIBK [8,11]. Therefore, the use of bifunctional catalysts of the Pt or Pd/H[Al]ZSM5 type [7–9,12] has made it possible to synthesize MIBK in one apparent stage and with 65–85% selectivity. The chemical reaction leading to the MIBK formation in this process is accompanied by a collateral chemical transformation by means of which propane is formed. This latter product is favorably formed as a function of an increase in the hydrogen partial pressure and/or the number of metallic centers dispersed over the support [9]. As already described [8,9,12], this catalytic behavior results from the acetone hydrogenation over the metallic centers, which leads to the formation of isopropanol; this, in turn, is dehydrated over the acidic sites of the zeolite support, generating propene, an olefine that is finally hydrogenated over the metallic centers to form propane.

This work is mainly aimed at preparing catalysts that may decrease propane formation rate without significantly modifying MIBK formation rate. In this regard, attempts were made to modify the metal phase of the bifunctional Pt/H[Al]ZSM5 catalyst by means of the controlled addition of an IB-group metal, copper in this case, with the aim of preparing PtCu/H[Al]ZSM5-type catalysts for the passiva-

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tion of the platinum hydrogenating activity towards hydrogenation of the acetone carbonyl double bond (C=O) but without altering its ability to hydrogenate the olefinic double bond (C=C) of the mesityl oxide (MO) intermediate.

2. Experimental

A ZSM5 zeolite was synthesized by means of the method proposed by Guth *et al.* [13]. The solid obtained was calcined at 500 °C in the presence of air to eliminate the orientating agent, and exchanged with a 1 M NH_4NO_3 solution. Then it was again calcined in the presence of dry air at 500 °C for 6 h. The synthesized zeolite was assessed by means of DRX, nitrogen adsorption at -196 °C and submitted to chemical analysis using the atomic absorption technique.

The results of the solid assessment suggest that this is a high purity and crystallinity ZSM5 zeolite, with 387 m^2/g of specific surface area (SSA) and a Si/Al atomic ratio equal to 50. The H[Al]ZSM5 zeolite (Si/Al = 50) was used as a support in the preparation of a series of bifunctional bimetallic catalysts of the PtCu/H[Al]ZSM5 type (Si/Al = 50) with a constant platinum percentage equal to 0.50 wt% and a variable copper content, ranging from 10 to 75 wt% of the supported platinum content.

Bifunctional bimetallic catalysts were prepared using the exchange-impregnation method [14], which allowed us to introduce platinum and copper amounts that were very close to those desired, using $Pt(NH_3)_4Cl_2$ and $Cu(NO_3)_2{\cdot}5H_2O$ as precursor salts. The methodology employed is described below:

(i) Bifunctional monometallic 0.50Pt/H[Al]ZSM5 catalysts (0.50 wt% platinum) and 0.50Cu/H[Al]ZSM5 (0.50 wt% copper) were prepared using the exchange-impregnation method. Once dried at 105 °C in the stove over night, they were calcined under dry air flow at 300 °C (for 6 h) and then reduced under hydrogen atmosphere at 500 °C (for 6 h).

(ii) Then different copper amounts (10, 25, 50, and 75 wt% of platinum) were introduced to the reduced and calcined 0.50Pt/H[Al]ZSM5 catalyst using solutions with the proper concentration of the $Cu(NO_3)_2{\cdot}5H_2O$ salt.

(iii) The solids prepared and dried at 105 °C in the stove were then calcined in dry air flow at 300 °C and reduced under hydrogen atmosphere at 500 °C for 6 h.

The series of bifunctional monometallic and bimetallic catalysts prepared was assessed by means of the atomic absorption technique, which allowed us to quantify both the platinum as well as copper content supported for each one of the solids prepared. Dispersion of the supported metallic phase for each catalyst was assessed by means of hydrogen chemisorption. On the other hand, dispersion of the metallic phase supported over the 0.50Pt–0.250Cu/HZSM5 catalyst was assessed by means of the technique of transmission electronic microscopy (TEM), using a Jeol-100 CXII microscope, it thus being possible to confirm the results obtained with hydrogen chemisorption. In addition, two of the catalysts of the series (0.50Pt/HZSM5 and 0.50Pt–0.250Cu/HZSM5) were characterized by means of electronic paramagnetic resonance spectroscopy (EPR) at room temperature using a Varian spectrometer, E-ling X-band, operating under a TE_{102} mode.

The hydrogenating activity of the catalysts was assessed using toluene hydrogenation as a reaction model. This reaction was carried out in a fixed-bed dynamic reactor at 110 °C, 1 atm, H_2/toluene molar ratio = 4 and WHSV = 21.5 h^{-1} [9]. A similar reactor was used for the acetone transformation over these catalysts, at 160 °C, 1 atm, acetone/H_2 molar ratio = 3 and WHSV (weight of reactant injected per weight of catalyst per hour) ranging between 9.4 and 38 h^{-1}. The reactor effluents in this case were in-line injected and analyzed in an HP-6890 chromatograph equipped with a 30 m CP-sil-5CB column.

3. Results and discussion

Recent research [7–9,14,15] allows us to state that the synthesis of the important MIBK solvent has lately been carried out in a single apparent stage from acetone and in the presence of hydrogen, using bifunctional catalysts of the Pt or Pd type, supported over acid or basic solids. However, this novel process has some drawbacks, such as the presence of a collateral reaction that permits the formation of large proportions of propane (Hc), which results in a decrease in MIBK selectivity. Therefore, we have considered the possibility of using bifunctional bimetallic catalysts, prepared according to the already described methodology, to try to direct this chemical transformation preferentially towards the MIBK formation.

Specific surface area (SSA) of the calcined and reduced solids was assessed and was found to range between 350 and 370 m^2/g (table 1), meaning that the supported metallic phase does not plug or block the microporosity of the supporting solid.

Platinum and copper content in these solids was also determined using the atomic absorption method and the results reached (table 1) are very close to the theoretical ones and fully reasonable given the methodology used to prepare the catalysts. Dispersion of the supported metallic phase of these catalysts was determined by means of the hydrogen chemisorption technique (results in table 1). However, we have characterized the 0.50Pt–0.250Cu/HZSM5 catalyst through TEM (figure 1), and dispersion in its supported metallic phase was close to 50%, a result that is well in agreement with the results reported in table 1. This suggests that the values obtained by means of the hydrogen chemisorption method do not seem to be overestimated.

3.1. Toluene hydrogenation

Hydrogenating and dehydrogenating ability of the catalysts under study, which depends on the number of active and

Table 1

Physicochemical characteristics of the series of monometallic and bimetallic bifunctional catalysts prepared. Pt (%), Cu (%), wt% of platinum and copper determined by means of atomic absorption. $X(\mathrm{Cu})$: copper atomic fraction present in every catalyst. SSA: specific surface area. $D(\mathrm{H/Pt})$ (%): platinum dispersion determined by hydrogen chemisorption. $A(\mathrm{H}^0)$: activity in toluene hydrogenation extrapolated at zero time

Catalyst	Pt (%) exp.	Cu (%) exp.	$X(\mathrm{Cu})$ exp.	SSA (m^2/g)	D (%) H/Pt	$A\mathrm{H}^0$ (mmol/h g)
0.50Pt/H[Al]ZSM5	0.49	–	0	370	76	18.5
0.50Pt–0.05Cu/H[Al]ZSM5	0.48	0.04	0.20	371	68	11.3
0.50Pt–0.125Cu/H[Al]ZSM5	0.50	0.12	0.42	362	56	6.0
0.50Pt–0.250Cu/H[Al]ZSM5	0.48	0.24	0.60	355	48[a]	3.5
0.50Pt–0.375Cu/H[Al]ZSM5	0.49	0.38	0.70	358	38	0.4
0.50Cu/H[Al]ZSM5	–	0.47	1.00	366	–	0

[a] Catalyst assessed by means of TEM.

accessible metallic centers of the solids [8,9] has been determined through their activity in toluene hydrogenation extrapolated at zero time (results in table 1). Table 1 shows that both dispersion in the platinum metallic phase as well as activity in toluene hydrogenation extrapolated at zero reaction time ($A(\mathrm{H}^0)$) decrease as copper atomic fraction in the catalysts increases ($X(\mathrm{Cu}) =$ number of Cu atom moles/number of Cu atom moles $+$ number of Pt atom moles). These results imply that when $X(\mathrm{Cu})$ is increased from 0.00 up to 0.70 a drastic fall of approximately 98% is observed in the toluene hydrogenation ability of these catalysts. However, the decrease in the dispersion of the supported platinum amounts only to 50% for the same range of $X(\mathrm{Cu})$ in the series of catalysts prepared. These results suggest the presence of an electronic effect which could probably appear combined with a geometric effect [16,17]. Therefore, to verify these results we have determined the values of the turnover number (TOF) in the toluene hydrogenation reaction for each catalyst in the series. These values were graphically represented as a function of $X(\mathrm{Cu})$ (figure 2).

Figure 2 shows that TOF continuously decreases as $X(\mathrm{Cu})$ increases, which basically confirms the presence of an electronic effect. However, we wish to state clearly that these results do not exclude the existence of a geometric effect, which could be acting concurrently with the electronic effect, but never alone, because otherwise it would cause activity per platinum atom to remain constant and this is not observed in figure 2. On the other hand, the assessment of the 0.50Pt/HZSM5 and 0.50Pt–0.250Cu/HZSM5 catalysts by means of the EPR technique allows us to demonstrate the

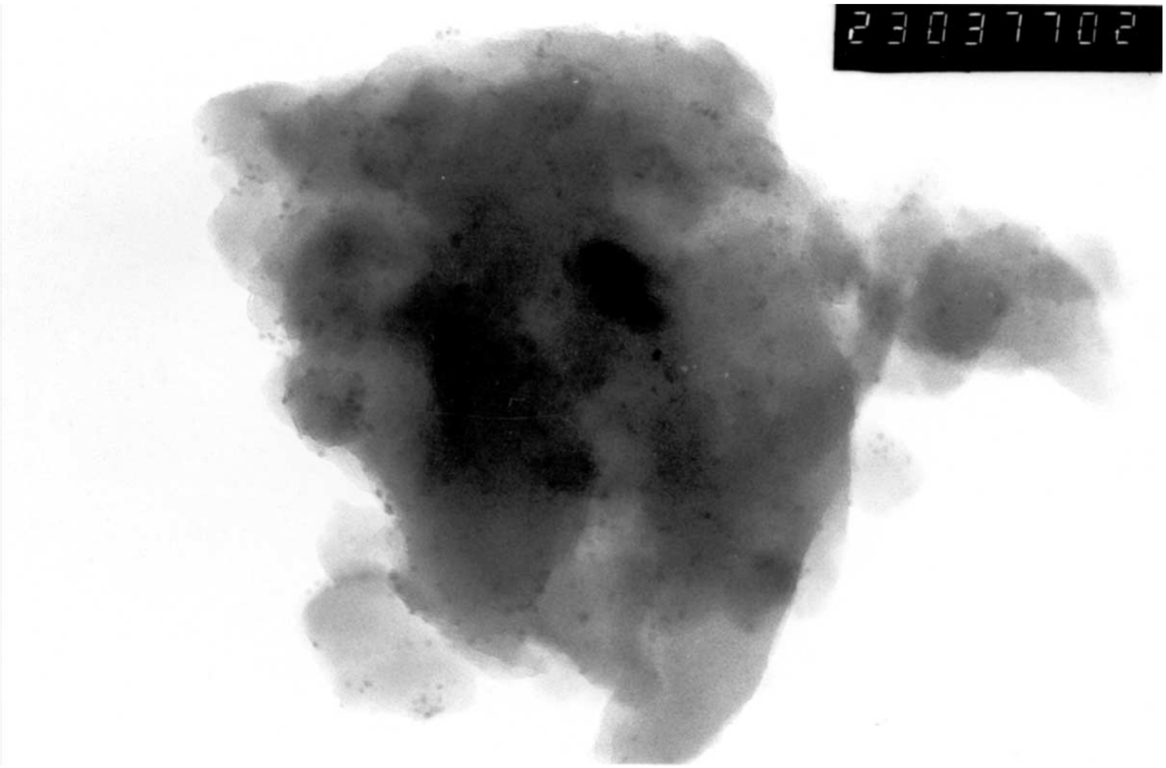


Figure 1. TEM micrograph for 0.50Pt–0.250Cu/HZSM5 catalyst, where 1 cm corresponds to 20 nm.

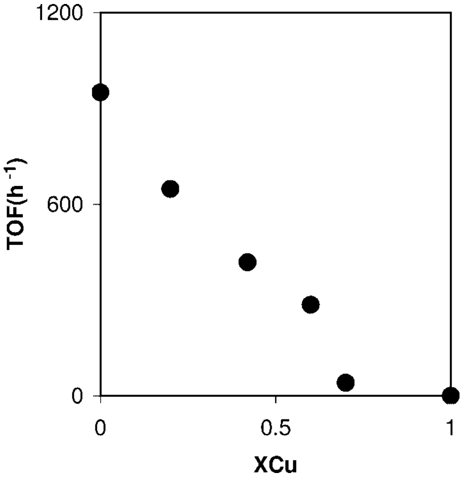


Figure 2. Evolution of turnover number (TOF) as a function of X(Cu), for the toluene hydrogenation reaction at 110 °C, 1 atm, $P(H_2)/P$(toluene) = 4, and WHSV = 21.5 h^{-1}.

presence of different magnetic environments for each catalyst, just as can be observed in figure 3. This suggests the existence of a number of unpaired electrons which are different for each catalyst, which could mean the presence of an electronic effect. However, given the presence of the signal characteristic of metallic copper in the EPR spectrum for the 0.50Pt–0.250Cu/HZSM5 catalyst, the existence of a phenomenon of the geometric type also seems very likely; these results would be in complete accord with the TOF development as a function of X(Cu).

3.2. Acetone transformation

3.2.1. Activity

Acetone transformation over these catalysts has been carried out under standard conditions and at variable WHSV. The decrease in the initial global activity in acetone transformation (A_0) with the increase in X(Cu) can be seen in figure 4. Also a 25% decrease in the initial global activity (A_0) is observed in all catalysts with $X(Cu) < 0.40$ and a 70% decrease is found for those catalysts with $X(Cu) \gg 0.40$ *versus* that of the catalyst with $X(Cu) = 0.00$ (0.50Pt/H[Al]ZSM5).

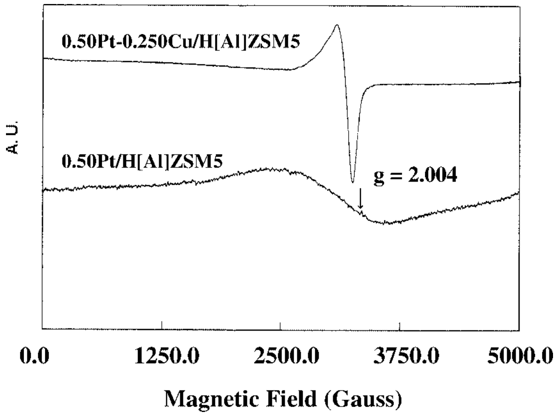


Figure 3. EPR spectrum of 0.50Pt/HZSM5 and 0.50Pt–0.125Cu/HZSM5 catalysts, taken under TE_{102} mode at room temperature.

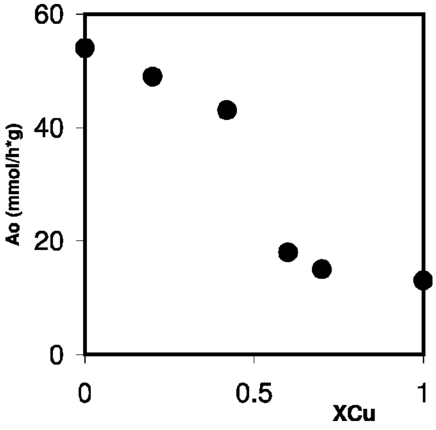
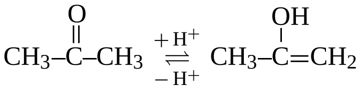


Figure 4. Evolution of initial global activity in ketone transformation as a function of X(Cu), at 160 °C, 1 atm, $P(Ac)/P(H_2) = 3$, and WHSV = 9.4 h^{-1}.

These results could be explained if we consider that the catalyst with $X(Cu) = 0.00$ can increase the velocity of a great deal of chemical reactions, among which all those requiring catalysis over acidic sites and metallic centers are found, for example acetone enolization and aldolization, dehydration of alcohols, such as isopropanol and diacetone alcohol, and hydrogenation of carbonyl and olefinic double bonds (C=O and C=C).

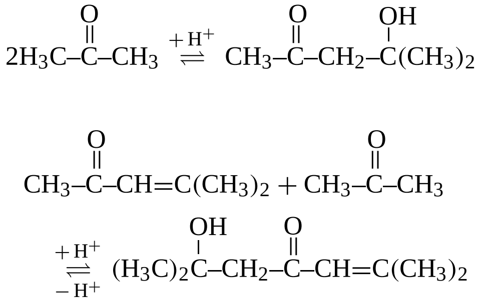
Reaction schemes for the aforementioned chemical transformations are shown below:

- Acetone enolization



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} CH_3-\overset{\overset{OH}{|}}{C}=CH_2$$

- Aldolization

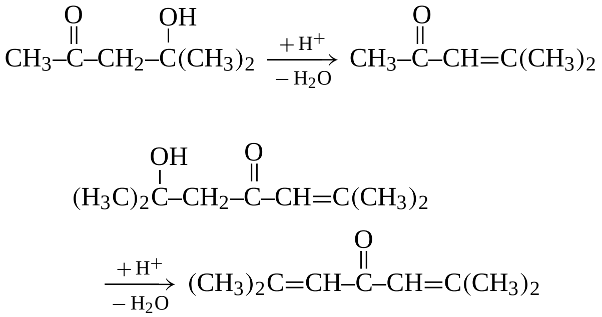


$$2H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \overset{+H^+}{\rightleftharpoons} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{OH}{|}}{C}(CH_3)_2$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2 + CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

$$\underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} (H_3C)_2\overset{\overset{OH}{|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2$$

- Dehydration

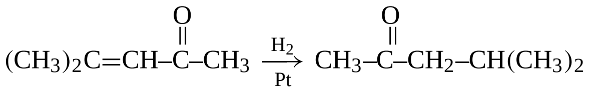


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{OH}{|}}{C}(CH_3)_2 \xrightarrow[-H_2O]{+H^+} CH_3-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2$$

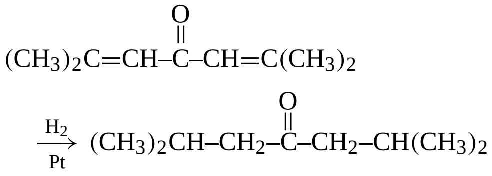
$$(H_3C)_2\overset{\overset{OH}{|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2$$

$$\xrightarrow[-H_2O]{+H^+} (CH_3)_2C=CH-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2$$

- Hydrogenation



$$(CH_3)_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow[Pt]{H_2} CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH(CH_3)_2$$



$$(CH_3)_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH{=}C(CH_3)_2 \xrightarrow[Pt]{H_2} (CH_3)_2CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH(CH_3)_2$$

However, once copper is introduced into the 0.50Pt/H[Al]ZSM5 catalyst, the velocity of many of these reactions is considerably restricted, as in hydrogenation of the carbonyl double bond, which undoubtedly might result from the fact that the PtCu/H[Al]ZSM5 catalyst is more and more inactive towards these reactions as X(Cu) increases, a catalytic behavior that should be associated to the copper–platinum interaction through the electronic and geometric effects [16,17]. However, the results obtained in toluene hydrogenation show that copper would basically be the one bringing about the largest variation in the supported phase.

3.2.2. Selectivity

Formation rate of the different products obtained in the acetone transformation considerably changes as copper content varies in the catalysts, as shown in figure 5, where the evolution of the initial formation rates of the methyl isobutyl ketone (r_0(MIBK)), propane (r_0(Hc)) and mesityl oxide (r_0(MO)) is presented as a function of X(Cu).

Figure 5 shows that initial propane formation rate (r_0(Hc)) is permanently decreasing as a function of the X(Cu) increase to such an extent that when this fraction value augments from 0.00 up to approximately 0.40, an 80% decrease is observed in r_0(Hc); this undoubtedly is due to the fact that the carbonyl double bond in the acetone is less and less hydrogenated as X(Cu) increases, which could mean that the formation of isopropanol and propene could be limited, intermediates leading to paraffin formation. Now, this catalytic behavior in the acetone transformation is perfectly consistent with the modification in the hydrogenating ability of the catalysts as a result of the increase in X(Cu). This phenomenon could be due to an electronic effect of copper toward platinum.

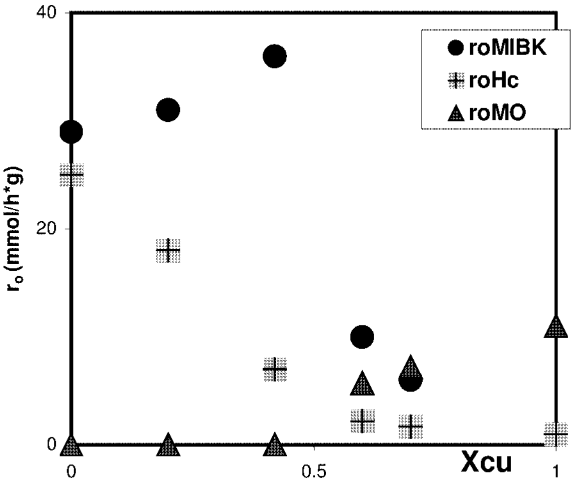


Figure 5. Evolution of initial formation rates of the products obtained (r_0(MIBK), r_0(Hc), and r_0(MO)) as a function of X(Cu), at 160 °C, 1 atm, $P(\mathrm{Ac})/P(\mathrm{H_2}) = 3$, and WHSV = 9.4 h^{-1}.

Initial formation rate of MIBK (r_0(MIBK)) first increases and then decreases as X(Cu) is higher, as can be observed in figure 5. It can be clearly seen that r_0(MIBK) initially shows a 20% increase as X(Cu) goes from 0.00 to approximately 0.40; but when the copper atomic fraction in the catalysts exceeds this limit ($X(\mathrm{Cu}) \gg 0.40$), an r_0(MIBK) decrease up to 50% is observed in the catalyst with $X(\mathrm{Cu}) = 0.70$. These results apparently suggest that metallic centers necessary for the hydrogenation of the MO olefinic double bond (C=C) are not the same required to hydrogenate the acetone carbonyl double bond (C=O), because r_0(MIBK) and r_0(Hc) increase and decrease respectively for the range of copper atomic fractions considered ($0.00 < X(\mathrm{Cu}) < 0.40$). Figure 5 also shows that for all of the catalysts with $X(\mathrm{Cu}) < 0.40$, the mesityl oxide initial formation rate (r_0(MO)) is zero, whereas it markedly increases for every solid with $X(\mathrm{Cu}) \gg 0.40$.

These results are completely consistent with those discussed before, because all of the catalysts with $X(\mathrm{Cu}) < 0.40$ are capable of hydrogenating the MO olefinic double bond generated, transforming it into MIBK, which explains the increase in r_0(MIBK). In addition, the hydrogenation reaction of the MO olefinic double bond considerably decreases, which explains the r_0(MO) increase when X(Cu) increases beyond 0.40. This implies that the metallic centers of the bimetallic catalysts with $X(\mathrm{Cu}) < 0.40$ are basically influenced by the electronic effect of copper on platinum, which explains why these metallic centers might be more selective towards the hydrogenation of the MO olefinic double bond; this can be seen in the relationship of the initial MIBK and propane formation rates ($r_0(\mathrm{MIBK})/r_0(\mathrm{Hc})$), which increases from 1 up to 6 when X(Cu) changes from 0.00 to approximately 0.40. In contrast, metallic centers of the bimetallic catalysts with $X(\mathrm{Cu}) \gg 0.40$ appear to be more influenced by a geometric effect, because solids, with an increase in X(Cu), exhibit a behavior similar to that of an acid catalyst, *i.e.*, platinum particles seem to be more coated by copper, and therefore those reactions requiring metallic catalysis are the most affected.

3.2.3. Stability

We have determined catalytic stability for the series of catalysts prepared, and it has been expressed as a function of residual activity (A_r, fraction of initial global activity of the catalyst once this has been used for 150 min in the reaction). Also we have determined the coke content (expressed as %C) and the nature of the carbonous residues deposited over the 0.50Pt/H[Al]ZSM5 ($X(\mathrm{Cu}) = 0.00$),

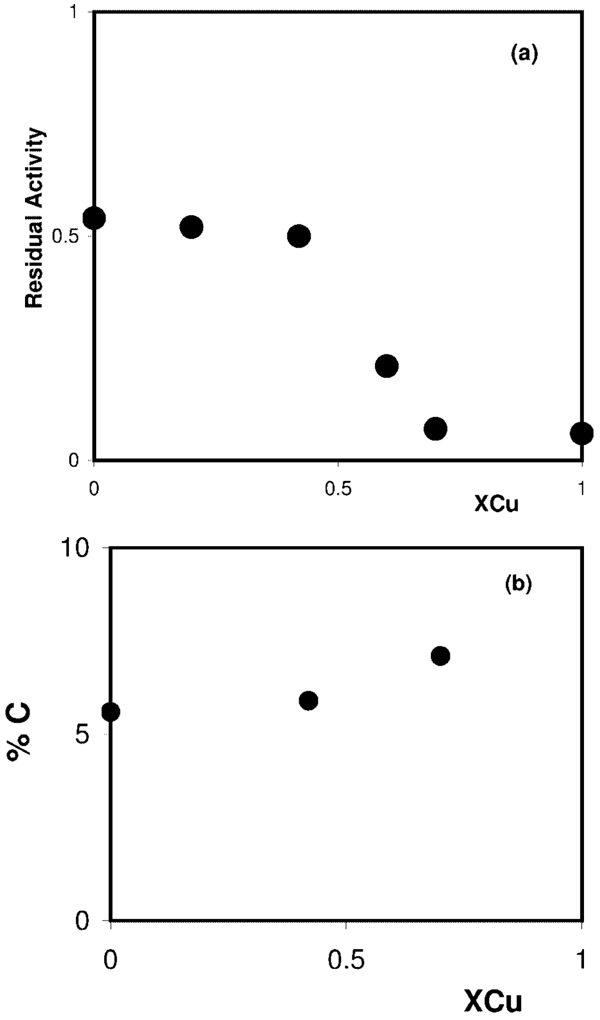


Figure 6. Evolution of residual activity (a) and coke content (expressed as %C) as a function of X(Cu) (b), at 160 °C, 1 atm, $P(\mathrm{Ac})/P(\mathrm{H_2}) = 3$, and WHSV $= 9.4\ \mathrm{h}^{-1}$.

0.50Pt–0.125Cu/H[Al]ZSM5 (X(Cu) $= 0.42$) and 0.50Pt–0.375Cu/H[Al]ZSM5 (X(Cu) $= 0.70$) catalysts while they were used in the chemical transformation under study.

Residual activity (A_r) and the coke content deposited over the solids has been graphically represented as a function of X(Cu) (figure 6 (a) and (b)).

We can see in figure 6(a) that all of the catalysts with X(Cu) < 0.40 have similar catalytic stability, close to 0.60. However, when X(Cu) exceeds 0.40, these solids' stability is drastically reduced, which might be related to their low hydrogenating activity. This explains why high MO concentrations are observed during the acetone transformation over these catalysts (X(Cu) $\gg 0.40$). Now, as a consequence of the high concentrations of α-β unsaturated ketone (MO) and propanone and of the existence of active acidic sites over the catalytic surface, the presence of the aldolization reaction is favored among these ketones, implying the formation of high volume and molecular weight products with difficult diffusion throughout the microporous HZSM5 structure. This explains why these molecules are normally held in the inner structure, contributing to the further deactivation process of those catalysts.

Table 2
Evolution of the coke nature obtained as a function of X(Cu)

Catalyst	X(Cu)	Coke nature
0.50Pt/H[Al]ZSM5	0.00	ISP $\cong$ PAB
0.50Pt–0.125Cu/H[Al]ZSM5	0.42	ISP $\gg$ PAB
0.50Pt–0.375Cu/H[Al]ZSM5	0.70	ISP

Therefore, to assess the correlation between content and nature of the deposited coke and the residual activity of the solids after 150 min use in the reaction [9], we have graphically represented the evolution of the coke content (%C) as a function of X(Cu) (figure 6(b)). In this figure we can clearly observe that coke content as well as residual activity show no significant variation for those catalysts with X(Cu) < 0.40, whereas for the catalyst with X(Cu) $= 0.70$ a 30% increase is observed in the amount of carbonous residues deposited over it, which can be perfectly correlated to its higher loss in catalytic stability (figure 6(a)). We also analyzed the nature of the carbonous residues deposited over the three catalysts considered (X(Cu) $= 0.00$, 0.42, 0.70), through the CPV-SM coupling. The results obtained show that the coke nature basically consists of isophorone (ISP) and polyalkylbenzenes (PAB), and significantly depends on X(Cu) in the catalyst, as can be seen in table 2.

According to this table, composition of the carbonous residues is fully consistent with the main reactions taking place in each catalyst under study, because the isophorone formation requires an acid catalysis and the formation of polyalkylbenzenes a bifunctional one [9].

4. Conclusions

The turnover number (TOF) in the toluene hydrogenation reaction is continuously decreasing as a function of an increase in X(Cu) in the series of PtCu/HZSM5 catalysts, implying the presence of an electronic effect between Pt and Cu. Total initial activity in acetone transformation as well as catalytic stability relatively vary with an increase in X(Cu) for those catalysts with X(Cu) < 0.40. However, formation rates of the MIBK and Hc products (r_0(MIBK), r_0(Hc)) increase and decrease, respectively, leading us to think that the metallic centers necessary for the hydrogenation of the MO olefinic double bond (C=C) are different from those required for the hydrogenation of the propanone carbonyl double bond (C=O).

Acknowledgment

Financial support by the EC within the International Scientific Cooperation EC-ALA/MED Countries (Contract CI1*CT94-0044) is gratefully acknowledged. The authors thank Dr. Delfin Moronta, Fac. Ciencias-UCV, for performing the EPR.

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