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Influence of silver on the catalytic activity of Cu-ZSM-5 for NO SCR by propane. Effect of the presence of water and hydrothermal agings

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The effect of silver on the activity and hydrothermal stability of Cu-ZSM-5 for NO_x reduction with C_3H_8 under oxidizing and wet conditions has been investigated. The addition of silver as a cocation to Cu-ZSM-5 catalysts decreases the reversible inhibition by water occurring under catalytic conditions when the temperature does not exceed 773 K. Furthermore, it suppresses the irreversible deactivation observed when the reaction is performed up to 873 K. In effect, the Cu–Ag-ZSM-5 solids are more resistant to the dealumination induced by the acids formed by reactions between NO, O_2 and H_2O than the Cu-ZSM-5 ones. The presence of silver provides also an higher hydrothermal stability under an (air + 10 vol% H_2O) mixture if the temperature does not exceed 973 K. The catalytic activity and the deactivation behaviour are dependent on the concentration of silver and copper and more especially on the preparation procedure.

Keywords: SCR NO_x, selective reduction, Cu-ZSM-5, Cu–Ag-ZSM-5, thermal stability, water tolerance, cocation effect, catalyst deactivation

1. Introduction

Cu-MFI solids are active for the selective reduction of NO by hydrocarbons [1–6], but the activity strongly decreases with the presence of water in the feed and the thermal stability is rather low. Their use for treatment of emissions from diesel and lean-burn engines is thus limited [7,8]. In previous works, we have shown that the rate of NO reduction into N_2 is directly connected to the number of isolated Cu^{2+}/Cu^{+} ions located in the zeolite structure [9–11]. In addition, aging treatments, under an (air + 10 vol% H_2O) mixture between 923 and 1173 K, lead to a decrease of this number of isolated Cu^{n+} ions [12]. At moderate temperatures the deactivation is mainly due to the partial migration of copper to inaccessible sites, the degradation (destruction of the framework, dealumination) of the zeolite itself being limited. At very high aging temperatures a part of the copper ions agglomerate into inactive CuO particles which remain accessible to CO [12].

In the literature, attempts to stabilize the Cu-MFI $DeNO_x$ catalysts have been performed by using various modifiers (La, Ce, Ba, Mg, ...) [13–16]. In our laboratory, we have also studied the effect of cocations in order to limit the migration and the subsequent agglomeration of exchanged copper ions. Silver has been chosen for various reasons: it is active by itself [17–19] and it possesses a relatively weak affinity for water. Furthermore, the oxide is relatively unstable and consequently the NO dissociation could be favoured on the metallic part. Among the cocations studied the silver cations have been found to be the most promising. The present paper deals with the activity, in the presence and in the absence of water, of fresh and hydrothermally aged Cu–Ag-ZSM-5 catalysts; the influences of the concentrations of silver and copper and of the preparation procedure have also been investigated.

2. Experimental

2.1. Catalysts

The starting material was a NH_4-ZSM-5 solid prepared by a NH_4Cl exchange of a commercial H-ZSM-5 zeolite from Degussa with a Si/Al ratio of 19 ($H_{4.8}Al_{4.8}Si_{91.2}O_{192}$).

Copper (or silver) was introduced by a conventional ion exchange of the NH_4-ZSM-5 zeolite. The zeolite was added to an aqueous solution of cupric nitrate (or silver nitrate) and the exchange was pursued for 2 h at 353 K under stirring. After centrifugation the obtained solids were washed several times so as to remove non-exchanged ions. After drying overnight at 383 K, the solids were calcined under an oxygen flow at 773 K (heating rate 1 $K\,min^{-1}$, plateau 8 h). In this paper these solids, prepared by exchange, are named Cu-ZSM-5 and Ag-ZSM. The calcination led to the formation of H-form zeolites. If one assumes that one Ag^{+} replaces one NH_4^{+}, 5.17 wt% Ag corresponds to an exchange level of 61% (protonated and hydrated zeolites). In high Si zeolites, the distance between two Al atoms seems too large to allow the neutralization of two monovalent anions by a single divalent cation. We have considered a

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$Cu(OH)^+$ cation linked to only one Al atom and to an extralattice oxygen introduced as OH, the $Cu(OH)^+$ formation occurring during the ion exchange process by hydrolysis of the water associated with the polyvalent cations [20].

Solids containing both Cu and Ag were prepared by successive exchanges with intermediate calcinations under O_2 at 773 K. Chemical analysis has shown that silver partly replaced copper in Cu-ZSM-5 and copper replaced a large part of silver in Ag-ZSM-5. For instance, a subsequent exchange by silver of the zeolite containing 1.3 wt% Cu led to a solid containing 0.26 wt% Cu and 3.26 wt% Ag. A subsequent exchange by copper of the Ag-ZSM-5 material containing 5.12 wt% Ag led to a sample containing 0.055 wt% Ag and 2.05 wt% Cu. However, by lowering the concentration of the copper solution as well as the number of exchanges, a solid containing 0.39% Ag and 1.78% Cu was prepared. According to the order of the exchanges the solids are named Cu(1)–Ag(2) or Ag(1)–Cu(2), the numbers referring to the firstly and secondly introduced cations.

In order to keep more silver in exchangeable positions, copper was also introduced by impregnation (no washing of the impregnated solid) of a zeolite previously exchanged by silver. The calcined Ag-ZSM-5 zeolite was added to the aqueous solution of copper nitrate and the suspension was kept for 1 h at 333 K under stirring. Water was removed under reduced pressure by using a rotary evaporator. After drying at 383 K and calcination under O_2 at 773 K as described above, the solid contained 4.05 wt% Ag and 1.89 wt% Cu. This solid is called Ag(1)–Cu(Imp), Imp being used for impregnation. In this case it is thought that copper is mainly deposited onto the zeolite but some solid-state ion exchange occurring during the calcination itself cannot be excluded [21].

Copper was also introduced by impregnation of a zeolite firstly exchanged by silver and previously treated under an hydrogen flow at 723 K (heating rate 2 $K\,min^{-1}$). This solid is named Ag(1,H_2)–Cu(Imp). Finally, a coimpregnation by silver and copper salts was also performed (Cu–Ag-COImp solid).

Table 1 gives the preparation method, the order of introduction and the Cu and Ag amounts for the various solids prepared.

Thermal treatments were performed at 923, 973 and 1023 K in the presence of water (10 vol% H_2O in air) for 24 h (total flow rate 10 $l\,h^{-1}$ for 5 g solid). Water was introduced and removed at high temperature.

2.2. Catalytic activity measurements

Catalytic measurements were made using 100 mg catalyst diluted with 400 mg of inactive α-Al_2O_3 in a fixed-bed flow reactor, as already described [9–12,22]. The typical gas mixture consisted of 2000 vpm NO, 2000 vpm C_3H_8, 10 vol% O_2, balance He, without or with 10 vol% water and a total flow rate of 10 $l\,h^{-1}$; vpm stands for ppm (v/v). In the absence of water in the reactants mixture, the temperature was increased from 423 to 773 K (or 873 K) (heating rate 4 $K\,min^{-1}$) and then decreased to 423 K (2 $K\,min^{-1}$). Water was then added at 423 K and the temperature increased and decreased again as above. The cycle was sometimes repeated after suppression of water in the mixture.

Table 1
Cu and Ag amounts and general behaviour during catalytic tests with the fresh solids.[a]

Solid	Cu (wt%)	Ag (wt%)	Deact.	N_2O
Cu-ZSM-5	1.96 and 1.77	0	yes	no
Ag-ZSM-5	0	5.12 and 4.18	no	yes
Cu(1)–Ag(2)	0.26	3.26	not done	yes
Ag(1)–Cu(2)	2.07	0.055	yes	no
Ag(1)–Cu(2)	1.78	0.39	no	no
Ag(1)–Cu(Imp)	1.89	4.05	no	no
Ag(1,H_2)–Cu(Imp)	1.85	3.82	no	no
Cu–Ag-COImp	1.87	0.84	small	no

[a] Imp: impregnation, COImp: coimpregnation. When not stated, the cations are introduced by exchange. H_2: treatment at 723 K under flowing H_2. (1) firstly introduced cation, (2) secondly introduced cation. Deact.: “yes” stands for a deactivation when the reaction is performed up to 873 K in the presence of water. N_2O: “yes” stands for a N_2O formation in the presence of water.

The analysis was performed by gas chromatography with two columns (Porapak and molecular sieves) and a TCD detector for CO_2, N_2O, O_2, N_2 and CO, and with a Porapak column and a flame ionisation detector for hydrocarbons. Moreover, on-line IR and UV analyzers were used for NO, N_2O, NO_2 and CO_2 analysis. The catalytic activities were calculated from the conversion of NO into N_2. The nitrogen balance was checked.

2.3. Physicochemical characterizations

Some solids were characterized before and after hydrothermal aging by various techniques: X-ray diffraction (Siemens diffractometer with Cu Kα radiation), SEM (Hitachi S800 with a 10 nm resolution), N_2 adsorption (BET and pore volume with a laboratory-made automatic apparatus), FTIR spectroscopy (framework vibrations and *in situ* adsorption of CO probe molecule), ^{27}Al MAS NMR (Bruker DSX 400).

For FTIR spectroscopy of adsorbed CO, the calcined or reduced samples were evacuated at 773 K for 1 h and the background spectrum was recorded after cooling at 300 K. After introduction of CO ($\approx$50 Torr) at 300 K as well as after evacuation at 300 K, the spectra were recorded as a function of time, as already described [9–12]. Spectra were recorded on a Nicolet Magan 550 spectrometer (2 cm^{-1} resolution). The optical densities of the bands were normalized by taking into account the amount of metal.

3. Results and discussion

The main products of reaction are N_2, CO_2 and NO_2. With our experimental conditions (2000 vpm NO, 2000 vpm C_3H_8, 10 vol% O_2, total flow rate 10 $l\,h^{-1}$)

NO_2 is formed in the pipes of the apparatus because of the gas-phase reaction of NO reacting with oxygen, as already noticed by Li and Hall [23]. Additional NO_2 is not formed on these zeolite-based solids.

In all the cases, the formation of N_2O is negligible (table 1), except for the fresh and aged solids rich in silver when the mixture contains water.

3.1. Catalytic activity of the fresh solids

With the Cu-ZSM-5 solids and without water in the mixture, we have already shown [12] that no deactivation is observed after temperature cycles to 773 or 873 K. Upon addition of water the activity clearly decreases but this effect is fully reversible if the water is suppressed and if the reaction temperature does not exceed 773 K. A competitive adsorption between H_2O and the reactants has been invoked. However, with a water-containing mixture, if the reaction temperature is raised up to 873 K, the catalyst is irreversibly deactivated (tables 1 and 2). We have previously assigned [12] this deactivation to the dealumination occurring, at 873 K, under the wet reactants mixture. This dealumination is due to an acid extraction [24], the acid formation occurring by reactions between H_2O, NO, O_2 and NO_2. We have already noticed, in the presence of water, that the nitrogen balance is not obtained (factor reaching 10–20%) and that the pH of the trapped water reaches 1. At the same temperature (873 K) no dealumination is observed by steaming, i.e., under the (air + 10% H_2O) mixture.

The behaviour of the solid containing a very small quantity of silver (0.055 wt%) is similar to that of Cu-ZSM-5 but the irreversible deactivation is limited in the case of the Cu–Ag-COImp sample. Furthermore, the deactivation induced by this nitric/nitrous acid formation is no more observed when silver is introduced by exchange in a sufficient amount. We will see in section 3.3 that the addition of silver does not suppress the acid formation but increases the stability of the zeolite, for reasons still unknown.

The Ag-ZSM-5 solid is, in the 423–723 K temperature range and in the absence of water, clearly less active than the Cu-ZSM-5 solid, but the activities become comparable at 773 K (table 2). In the case of Ag-ZSM-5 the conversion of NO into N_2 is not affected by water addition, probably because of the weak affinity of silver for H_2O. However, N_2O is detected above 673 K in the presence of water, the conversion of NO into N_2O reaching 12% at 773 K. The reason of this N_2O formation is unknown at the present time but we can notice that, with alumina and silica-supported precious metals [25], significant quantities of N_2O are formed during the selective reduction of NO by propane or propene, contrarily to copper-based catalysts. In fact, Ag-ZSM-5 and Ag/Al_2O_3 solids are effective for NO_x removal with oxidized hydrocarbons [17–19].

The behaviour of the solid containing only 0.26 wt% Cu and 3.26 wt% Ag is similar to that of Ag-ZSM-5 (table 1) but the N_2O formation is no more observed for solids containing both Ag and Cu, when the copper content reaches 1 wt%, even with high silver amounts. The behaviour becomes thus similar to that of a zeolite containing only copper.

Table 2
Conversions of NO into N_2 for the fresh solids in the absence and in the presence of water in the feed.[a]

Solid	T_{50}	$Conv_{623}$	Max.	$Conv_{773}$	$Conv_{873}$
Cu-ZSM-5 (1.96%)					
Without H_2O	598	63	66% at 638	58	38
With H_2O[b]	–	2	36% at 823	35	13
Suppression of H_2O	593	59	60% at 633	30	17
Ag-ZSM-5 (5.12%)					
Without H_2O	738	13	no	57	
With H_2O	738	12	no	54	
Ag(1)–Cu(2) 1.78% Cu–0.39% Ag					
Without H_2O	601	60	74% at 633	67	52
With H_2O	–	19	41% at 773	41	23
Suppression of H_2O	603	58	71% at 633	64	50
Ag(1)–Cu(Imp) 1.89% Cu–4.05% Ag					
Without H_2O	578	56	58% at 638	52	23
With H_2O	–	0	no	28	17
Suppression of H_2O	583	55	57% at 643	50	21

[a] T_{50}: light-off temperature (K) (temperature to reach 50% conversion). $Conv_{623}$, $Conv_{773}$, $Conv_{873}$: conversions at 623, 773, 873 K. Max.: maximum NO conversion at T (K).

[b] Because of the deactivation observed in the presence of water in the feed stream at 873 K, the values here reported are measured during the decrease in temperature.

The comparison of the activities shows that, without water, the activity of the solid prepared by successive exchanges (Ag(1)–Cu(2), 1.78 wt% Cu and 0.39 wt% Ag)) is similar to that of Cu-ZSM-5. However, in the presence of water, the introduction of silver allows to keep a better activity, in particular after a treatment up to 873 K under the wet reactants mixture (table 2). The solid prepared by coimpregnation (Cu–Ag-COImp, 1.87% Cu and 0.84% Ag) and the solid prepared by copper impregnation of the previously silver-exchanged one (Ag(1)–Cu(Imp), 1.89% Cu and 4.05% Ag) have similar activities and are slightly less active than the solid prepared by successive exchanges.

In all the cases, the solid for which an intermediate H_2 treatment has been performed after the exchange by the silver salt and before the impregnation by the copper salt (Ag(1,H_2)–Cu(Imp), 1.85% Cu and 3.82% Ag) is the most active one. Without water in the feed it is slightly more active than Cu-ZSM-5, the NO into N_2 conversion reaching 78% at 623 K and 68% at 773 K, instead of 63 and 58%, respectively. In the presence of water the activity is strongly increased by the addition of silver, the NO into N_2 conversion being equal to 24% at 623 K and 52% at 773 K, instead of 2 and 35%, respectively. The performances of this H_2-treated solid are higher than those of the same solid without an intermediate H_2 treatment.

The calcination temperature, 473 or 773 K, after the copper impregnation on the H_2-treated silver-exchanged zeolite has no effect on the catalytic behaviour.

Table 3
Conversions of NO into N_2 for the aged solids in the absence and in the presence of water in the reactant mixture.[a]

Solid	$Conv_{623}$	Max.	$Conv_{773}$	$Conv_{873}$
Cu-ZSM-5 (1.96%)				
Aged 923 K. Without H_2O	20	54% at 810	50	23
Aged 923 K. With H_2O[b]	0	44% at 810	38	15
Aged 973 K. Without H_2O	0	28% at 833	19	7
Aged 973 K. With H_2O[b]	0	13% at 773	13	0
Ag-ZSM-5 (5.12%)				
Aged 923 K. Without H_2O	16		20	
Aged 923 K. With H_2O	6		15	
Ag(1)–Cu(2) 1.78% Cu–0.39% Ag				
Aged 923 K. Without H_2O	15	43% at 843	33	29
Aged 923 K. With H_2O	7	30% at 813	25	16
Aged 973 K. Without H_2O	12	37% at 846	20	16
Aged 973 K. With H_2O	0	22% at 833	12	10

[a] $Conv_{623}$, $Conv_{773}$, $Conv_{873}$: conversions at 623, 773, 873 K. Max.: maximum NO conversion at T (K).

[b] Because of the deactivation observed in the presence of water in the feed stream at 873 K, the values here reported are measured during the decrease in temperature.

3.2. Catalytic activity of the (air + 10 vol% H_2O)-treated solids

In almost all the cases, the activities strongly decrease with the aging treatments (tables 2 and 3). When water is added to the mixture, the activities decrease again but to lower extents than in the case of the fresh solids. For the aged solids containing no silver or only low amounts of silver, an irreversible deactivation under the wet reactants mixture is still observed if the reaction is performed up to 873 K (table 3). As for the fresh solids, this deactivation is attributed to a dealumination induced by the acid component arising from the reaction of H_2O with NO_2 formed in the pipes of the apparatus. With an acidic medium the dealumination occurs at a lower temperature than with the (air + 10 vol% H_2O) mixture.

N_2O is detected, in the presence of water, in the same cases as with the fresh solids, i.e., without copper or with low amounts of copper.

The Ag(1)–Cu(2) sample containing 1.78% Cu and 0.39% Ag remains, after aging at 973 K, a little more active than the solids without silver (table 3). This is not observed with the Cu–Ag-COImp and Ag(1)–Cu(Imp) solids.

The Ag(1,H_2)–Cu(Imp) solid, after aging at 973 K, has a relatively high activity, especially at high temperatures, even in the presence of water (figure 1). In the aged state this solid is the most active one. At 773 K, the NO conversion into N_2 reaches 70% in the absence of water and 48% in the presence of water, instead of 19 and 13% for the 973 K-aged Cu-ZSM-5 sample. The activity of the Ag(1,H_2)–Cu(Imp) solid decreases strongly, however, when the aging temperature reaches 1023 K; it is thus equal, at 773 K, to 32% without water and to 27% with water in the feed. Increasing the aging temperature from 973 to 1023 K induces a strong decrease in activity.

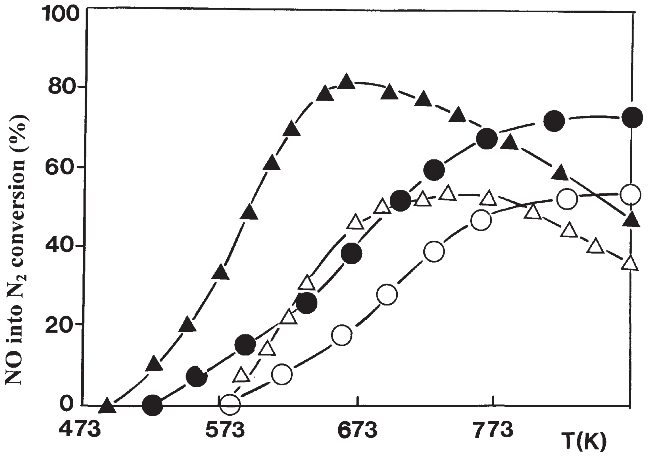

Figure 1. NO conversion into N_2 as a function of the temperature, in the presence and in the absence of water, for the fresh and 973 K-aged Ag(1,H_2)–Cu(Imp) solid. (▲) Fresh catalyst without water in the feed, (△) fresh catalyst with water in the feed, (●) aged catalyst without water in the feed, (○) aged catalyst with water in the feed.

In an attempt to discriminate the effects of the concentrations and/or the preparation procedure, we can note, as well as for the fresh and 973 K-aged solids, that:

- whatever the preparation procedure, the deactivation induced by the acid formation and the N_2O formation are suppressed if silver and copper are introduced in sufficient amounts, respectively;
- however, the preparation procedure clearly influences the activity in the presence of water in the stream.

The preparation procedure is also very important to maintain an activity after an hydrothermal aging treatment at 973 K.

Let us note that we have impregnated a 973 K-aged Cu-ZSM-5 sample with copper nitrate, the idea being to keep highly dispersed copper after a second hydrothermal treatment at 973 K. This attempt has been unsuccessfull, the copper migration (and so on the deactivation) being not inhibited.

3.3. Physico-chemical properties

The properties of Cu-ZSM-5 (1.77% Cu) and of (Ag (1,H_2)–Cu(Imp)) have been studied.

After aging at 923, 973 and 1023 K, there is no modification of the X-ray patterns. Neither a clear destruction of the zeolite framework, neither a loss of crystallinity and nor CuO have to be considered.

The aging treatments cause a decrease in the micropore volume and in the microporous surface. These decreases are similar for the two solids, the microporous surface decreasing from 287 to 216 m^2/g and from 281 to 210 m^2/g, respectively, upon a 973 K-aging.

The aging treatments lead to a shift of the FT-IR bands due to the T–O vibrations of the zeolite lattice towards higher wavenumbers, which indicates a partial dealumination of the lattice. The variations remain, however, small

Table 4

Optical density (per gram solid) of the 2193 cm^{-1} band (CO adsorbed on Ag^+) and of the 2157 cm^{-1} band (CO adsorbed on Cu^+) after CO evacuation at room temperature for 1 h for the fresh and aged Cu-ZSM-5 (1.77%) and Ag(1,H_2)–Cu(Imp) solids.

Solid	O.D.	
	2193 cm^{-1}	2157 cm^{-1}
Cu-ZSM-5 fresh	0	56
Cu-ZSM-5 aged 973 K	0	14
Cu-ZSM-5 aged 1023 K	0	12
Ag(1,H_2)–Cu(Imp) fresh	2	45
Ag(1,H_2)–Cu(Imp) aged 973 K	16	26
Ag(1,H_2)–Cu(Imp) aged 1023 K	33	13

because of the low initial Si/Al ratio. The introduction of silver does not induce a clear difference, the 1226–1227 cm^{-1} band shifting to 1229–1230 cm^{-1} and the 1096 one to 1099 cm^{-1} upon aging at 973 K. After aging of the Ag(1,H_2)–Cu(Imp) sample at 1023 K, the bands reach 1232 and 1101 cm^{-1}, i.e., the dealumination becomes more important.

From the ^{27}Al NMR spectroscopy it is possible to follow the amounts of lattice and extra-lattice Al studying the signals corresponding to tetrahedral T_d Al (at around -55 ppm) and octahedral O_h Al (at around 0 ppm). The fresh and 923, 973, 1023 K-aged samples show only the signal of T_d Al and this signal is not clearly decreasing. Furthermore, there is no appearance of O_h Al. After treatment up to 873 K with the wet reactant mixture, the NMR signal of O_h Al appears in the case of Cu-ZSM-5 but not in the case of Ag(1,H_2)–Cu(Imp). This latter solid is more resistant to dealumination by an acid component than the first one. This agrees with the absence of deactivation.

In the case of Cu-ZSM-5 zeolites, it has been previously shown that the IR νCO bands belong to CO adsorbed on Cu^+ ions [20,26–29], these ions being generated by the reduction of Cu^{2+} ions under vacuum and/or by the probe itself [20]. Furthermore, the zeolite framework acts as a host for isolated Cu^{n+} ions (νCO bands of CO adsorbed on Cu^+ at 2152 and 2157 cm^{-1}, under CO and after evacuation at 300 K, respectively). After agings at 973 and 1023 K the absorbance of the 2157 cm^{-1} band decreases (table 4), i.e., some copper ions have migrated to positions inaccessible to CO [12]. The NO reduction rate into N_2 has been correlated with the number of isolated Cu^{n+} ions accessible to CO and detected by infrared spectroscopy [9–11].

In the case of Ag(1,H_2)–Cu(Imp), another band at 2193 cm^{-1} corresponding to CO adsorbed on Ag^+ is detected (figure 2). These CO/Ag^+ species are less stable than the CO/Cu^+ species and, after evacuation at 300 K, the intensity of the 2193 cm^{-1} band is much lower than the intensity of the 2157 cm^{-1} one. The assignment of the 2193 cm^{-1} band has been deduced from the study of the CO adsorption on the Ag-ZSM-5 zeolite, reduced or not. The calcined Ag-ZSM-5 solid presents this 2193 cm^{-1} band, the intensity of which decreases gradually upon evacuation at room temperature but the band is still observed after an overnight evacuation. By contrast, CO adsorbed on a reduced Ag-ZSM-5 solid is completely removed upon evacuation at room temperature.

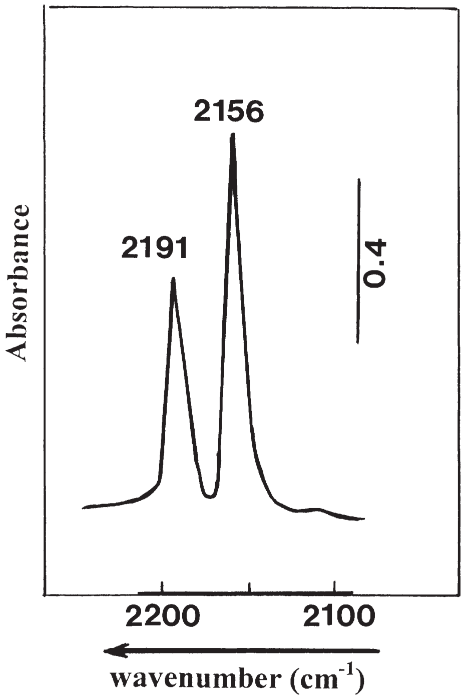

Figure 2. Infrared spectrum of CO irreversibly adsorbed after 1 h evacuation at 300 K on the 973 K-aged Ag(1,H_2)–Cu(Imp) solid.

During the aging treatments the intensity of the 2157 cm^{-1} band decreases while that of the 2193 cm^{-1} one increases (table 4). It might be supposed that some copper ions have migrated to inaccessible sites while silver ions were migrating to sites accessible to CO. However, the solid remains more active than the Ag-ZSM-5 one. Furthermore, the 2157 cm^{-1} band, i.e., the number of isolated Cu^{n+} ions accessible to gases, decreases in a lower extent in the presence of silver (factors 1.7 and 3.4 after agings at 973 and 1023 K, respectively) than without silver (factors 4 and 4.5) (table 4). The migration of copper to inaccessible sites is lowered by the introduction of silver.

4. Concluding remarks

It is possible to partly prevent the catalyst deactivation and in particular to decrease the inhibiting water effect by addition of silver as a cocation to Cu-ZSM-5. The preparation procedure (order of exchange, nature of the intermediate treatments, etc.) is an important factor. The fresh and aged silver-modified catalysts display high DeNO$_x$ activity in wet conditions, the reversible inhibition by water being diminished. The pre-exchange of the zeolite with silver prevents also the irreversible deactivation observed when the reaction is pursued, in the presence of water, up to 873 K. The Ag-modified solid recovers thus its dry-gas activity after removal of steam. The pre-exchange of silver into the zeolite provides also better catalytic performances after hydrothermal treatments with a (10 vol% H_2O in air) mixture if the temperature does not exceed 973 K.

The decrease in microporous volume and the dealumination remain very weak after the hydrothermal treatments with the (10 vol% H_2O in air) mixture up to 973 K, without or with silver. The deactivation is mainly due to a copper migration but this migration is partly inhibited for the pre-exchanged Ag zeolite. Furthermore, a migration of silver to accessible sites and a contribution of silver to the reaction is also possible. By treatment at 873 K under a wet reactants mixture ($NO–C_3H_8–O_2–H_2O$), i.e., in the presence of an acid component, the dealumination decreases by adding silver with the appropriate preparation procedure.

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