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Cu based zeolites: A UV–vis study of the active site in the selective methane oxidation at low temperatures

Pieter J. Smeets, Marijke H. Groothaert, Robert A. Schoonheydt *

Center for Surface Chemistry and Catalysis, K.U. Leuven, Kasteelpark Arenberg 23, B-3001 Leuven, Belgium

Abstract

An extensive series of 30 Cu exchanged zeolites and Cu impregnated silicas and aluminas have been tested in their capacities to stabilize the bis(μ-oxo)dicopper core. This core shows a remarkably activity towards methane, as it selectively hydroxylates methane into methanol at the low temperature of 125 °C. UV–vis spectroscopy is an easy approach to detect the presence of this bis(μ-oxo)dicopper core since it is characterized by an intense charge transfer band at 22 700 cm^{-1}. In this way it was found that after calcination, only the Cu exchanged zeolites ZSM-5 and MOR are capable of stabilizing this core. In addition, an optimum in the Si/Al ratio and in the calcination temperature were observed, indicating that this core requires a rather specific coordination environment. For ZSM-5, the optimal Si/Al ratio for bis(μ-oxo) dicopper core formation is between 12 and 30 and the amount of this core increases with increasing copper loading above Cu/Al = 0.2. Calcination in O_2 should be done at temperatures higher than 280 °C and lower than 700 °C. After reaction with methane at low temperature (150 °C), it was found that only Cu-ZSM-5 and Cu-MOR yielded methanol, whereas all the other Cu based materials yielded almost no methanol. At higher temperatures (200 °C) however, Cu-FER and Cu-BEA showed comparable methanol yields as Cu-ZSM-5 and also the methanol yield of Cu-MOR increased at this higher reaction temperature, indicating that a second not yet identified Cu-oxygen species is activated in the FER, BEA and MOR zeolites at higher temperatures.

Keywords: Bis(μ-oxo) dicopper core; Zeolites; Silica; Alumina; UV–vis spectra; Oxidation

1. Introduction

Cu-ZSM-5 is active in a wide range of reactions of nitrogen oxides, i.e. the (photo) catalytic decomposition of NO and N_2O, the catalytic reduction of NO with CO and hydrocarbons, and the selective catalytic reduction of NO with NH_3 [1]. So far, commercial deNO_x applications of Cu-ZSM-5 include (i) the high-temperature reduction of stationary NO_x emissions using NH_3 and (ii) lean NO_x reduction for diesel vehicles, as just recently communicated by Volvo [2]. While in the past 20 years generally a consensus is found on the catalytic performances, the identification of the active sites often remains a matter of debate [3,4]. In a recent study of our group it was found that calcined Cu-ZSM-5 samples with Cu/Al ratio >0.2 are characterized by an additional band in the UV–vis spectra at 22 700 cm^{-1}. Based on EPR, EXAFS and TEM studies together with the position of the UV–vis band at 22 700 cm^{-1}, it was concluded that these data could be assigned to the bis(μ-oxo)dicopper core (species **A** in Scheme 1) [5,6]. When testing these Cu-ZSM-5 samples for NO decomposition, a very strong correlation between the catalytic activity and the presence of the **A** core was found. It was proposed that the **A** core regulates the release of O_2, and thus the concomitant self-reduction of the copper sites, which is known to be the most difficult step in the catalytic NO decomposition.

The **A** core has so far been identified in homogeneous model complexes, mostly with multidentate N-ligands [7]. Thorough studies have been spent to this **A** core as it can easily interconvert with its peroxo-isomer, (μ-η^2:η^2-peroxo)dicopper (species **B** in Scheme 1), which is the active site in several enzymes. In hemocyanin, this **B** core regulates the transport of O_2 via the reversible binding of O_2 [8]. Taking into account that nature selected a Cu_2O_2 core for O_2 transport, it is not surprising that a copper dimer in Cu-ZSM-5 was found as active site for O_2 release.

Cu_2O_2 cores are also known for their mono-oxygenase activity. The **B** core is the active site in the enzyme tyrosinase where it hydroxylates monophenols to *o*-diphenols whereas the

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* Corresponding author. Tel.: +32 16 321592; fax: +32 16 321998.
E-mail address: Robert.Schoonheydt@biw.kuleuven.be (R.A. Schoonheydt).

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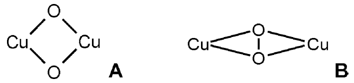

Scheme 1. (**A**) the bis(μ-oxo)dicopper core and (**B**) the (μ-η²:η²-peroxo)dicopper core.

A core is suggested as active site in the enzyme particulate methane monoxygenase (pMMO), which hydroxylates methane into methanol. As already one functional resemblance was found between the **A** core in zeolites and the **B** core in enzymes, being the release of O_2, we thought it might be worth to study the oxidation capacity of the **A** core in zeolites using methane as the substrate [9]. Using UV–vis we found that the 22 700 cm^{-1} absorption band disappeared upon contacting the O_2-activated sample with methane at 125 °C. However, no reaction products were found in a concomitant GC analysis of the reactor outlet. As product desorption might be a problem, the sample was extracted and methanol was found as the only product, as confirmed by GC, GC-MS and ^1H and ^{13}C NMR analyses. The high correlation between the intensity of the 22 700 cm^{-1} band and the extracted methanol yield strongly indicated that the **A** core is the active site in the selective methane oxidation. This reaction constitutes the second functional resemblance of Cu-ZSM-5 with the Cu_2O_2 cores in enzymes and homogeneous model complexes.

In this work, the interaction of the bis(μ-oxo)dicopper core with CH_4 was further investigated. First, it was tried to stabilize this interesting core in a wide range of other zeolites and also in silicas and aluminas, in order to understand the importance of the zeolite topology and Si/Al ratio. Second, the effect of high calcination temperatures on the formation of the **A** core was determined. In each of these topics, a relation is made between the (i) presence of the 22 700 cm^{-1} band and (ii) the methanol yield after extraction. Finally, with fiber-optic UV–vis, detailed information on both time and temperature scale is obtained on the formation and stability of the bis(μ-oxo)dicopper core in O_2, He or CH_4 atmosphere.

2. Experimental

2.1. Preparation of Cu^{2+} exchanged zeolites

In Table 1, the characteristics of all prepared Cu^{2+} zeolite samples are summarized. Zeolites were obtained from ALSI-PENTA, PQ-zeolites, Norton, Toyo Soda, Tricat Zeolites GmbH, Zeocat™ and ExxonMobil Chemical. Prior to Cu^{2+} exchange, the samples were exchanged with $NaNO_3$ (Fluka). For 1 g of zeolite, 150 mL deionized H_2O was used with 1 g of the $NaNO_3$ salt. The mixture was stirred at room temperature (RT) for 24 h, filtered and washed. This exchange procedure was repeated once (for the Na^+ form) or three times (for the non-Na^+ zeolites). After the Na^+ exchange, the samples were dried at 60 °C. The Na^+ zeolites were subsequently exchanged in an aqueous 10 mM Cu(II) acetate solution (Acros, Cu-acetate monohydrate) in analogy to the work of Iwamoto et al. [10] The amount of Cu^{2+} solution added to 1 g of zeolite is dependent on its Si/Al ratio and determined as such that in case of a full exchange a Cu/Al ratio of 0.5 would be obtained. The mixture was stirred for 24 h at RT, filtered and washed. This Cu^{2+} exchange was repeated three times for each zeolite sample. After the third exchange, the zeolites were dried in air at 110 °C. The as-prepared samples will be denoted as CX-*Y*-*Z* where X stands for the first letter of the zeolite (Z = ZSM-5, M = MOR, U = USY, Y = Y, B = *BEA, F = FER and E = EMT), *Y* represents the Si/Al ratio and *Z* the Cu/Al ratio. Cu and Al contents were determined by ICP analysis after the dissolution of the samples.

2.2. Preparation of Cu^{2+} impregnated silicas and aluminas

The silicas and aluminas were obtained from Grace and Merck and their characteristics are given in Table 2. Different amounts of Cu(II) acetate monohydrate (Acros) were dissolved in deionized water, and an amount of copper solution equal to the pore volume was used. Given the solubility of Cu(II) acetate in water (=72 g L^{-1}), it was impossible to load the materials

Table 1
Overview of the characteristics of the Cu^{2+} zeolites

Sample	Source	Topology	Si/Al	# mL 0.01 M Cu solution/g	Cu/Al	Cu wt.%
CZ-12-0.54	ALSI-PENTA	MFI	12	63	0.54	4.3
CZ-25-0.51	PQ-zeolites	MFI	25	32	0.51	2.0
CZ-30-0.47	ExxonMobil	MFI	30	25	0.47	1.5
CZ-77.5-0.55	PQ-zeolites	MFI	77.5	9.75	0.55	0.68
CZ-120-0.88	PQ-zeolites	MFI	120	6.3	0.88	0.77
CM-5.3-0.39	Norton	MOR	5.3	144	0.39	6.2
CM-8.8-0.50	TRICAT	MOR	8.8	78	0.50	5.1
CE-4-0.36	ExxonMobil	EMT	4	189	0.36	7.3
CF-6.2-0.42	Toyo Soda	FER	6.2	126	0.42	5.9
CB-9.8-0.50	ZEOCAT™	BEA	9.8	100	0.50	4.7
CY-2.7-0.45	ZEOCAT™	FAU	2.7	664	0.45	11
CU-13.5-0.32	PQ-zeolites	FAU	13.5	500[a]	0.32	2.3
CU-14.5-0.42	ZEOCAT™	FAU	14.5	500[a]	0.42	2.9
CU-27.5-0.34	PQ-zeolites	FAU	27.5	500[b]	0.34	1.2
CU-36.9-0.34	PQ-zeolites	FAU	36.9	500[c]	0.34	0.9

[a] In this case, the molarity of the Cu solution amounted to 0.001 M.
[b] In this case, the molarity of the Cu solution amounted to 0.6 mM.
[c] In this case, the molarity of the Cu solution amounted to 0.4 mM.

Table 2
Overview of the characteristics of the Cu^{2+} silicas and aluminas

Sample	Source	Al_2O_3 content (wt.%)	Pore volume (mL/g)	Cu wt.%
CS1-2.0	Grace nr9	0.6	1.48	2
CS1-4.0	Grace nr9	0.6	1.48	4.0
CS2-1.4	Grace silica	13	1.1	1.4
CS2-4.0	Grace silica	13	1.1	4.0
CS3-1.5	Grace SG239	–	1.14	1.5
CS3-4.0	Grace SG239	–	1.14	4.0
CS4-1.5	Grace SG432	–	1.20	1.5
CS4-4.0	Grace SG432	–	1.20	4.0
CA1-0.8	Merck γ-alumina	100	0.7	0.8
CA1-1.7	Merck γ-alumina	100	0.7	1.7

with high (4 wt.% Cu) Cu^{2+} loadings, thus the impregnation of these samples was performed in two steps. All samples were dried overnight at 110 °C. The as-prepared samples will be denoted as CX-*Y*-*Z* where X stands for silica (X = S) or alumina (X = A), *Y* is a numerical value (*Y* = 1–4) used to distinguish between the different samples and *Z* the Cu wt.%.

2.3. UV–vis–NIR spectroscopy

In situ UV–vis–NIR spectra of all overnight calcined Cu^{2+} samples (heating rate of 1 °C min^{-1} to 450 °C; 100% O_2, flow of 50 mL min^{-1}) were recorded in the diffuse reflectance mode (DRS) on a Varian Cary 5 UV–vis–NIR spectrophotometer according to the method described in Ref. [5].

UV–vis spectra were also collected during temperature treatments in O_2, He or CH_4 flow. Therefore a plug-flow reactor with optical fibre mounted on the outer surface of the quartz wall of the reactor was used as described in Ref. [9]. Typically, each spectrum is the result of the superposition of 500 scans each taking 50 ms, thus, one spectrum is obtained every 25 s.

2.4. Reaction with methane

Generally, the samples were calcined in O_2 as described in the previous section. In some cases the calcination temperature was altered, as clearly indicated in the text. After calcination, the sample was cooled in a closed O_2 atmosphere to RT and flushed with He (50 mL min^{-1}) for 1 min at RT. A mixture of 5% CH_4 in N_2 (25 mL min^{-1}) was passed over the sample while the latter was heated at a rate of 10 °C min^{-1} either to 150 or 200 °C as will be indicated in the text. After reaction, the zeolite samples were extracted in a water:acetonitrile mixture (1:1 v/v) for 20 h under vigorous stirring. The reaction conditions and the details of the extraction procedure and GC analysis are described in an earlier contribution [9].

3. Results and discussion

3.1. Treatment of the calcined Cu-ZSM-5 sample in He versus methane

While our previous operando UV–vis experiments dealt with the role of the **A** core in the decomposition of NO and N_2O, we used the set-up in this study to gain information on the formation of the **A** core in O_2 atmosphere and its stability when contacted with He or methane. Fig. 1(a) and (b) shows the UV–vis spectra of CZ-12-0.54 at 500 °C during an O_2–He and He–O_2 switch, respectively. In Fig. 1(a), the sample was treated in He after calcination in O_2 at 500 °C. Apart of the d–d transitions of isolated Cu^{2+} ions at 14 000 cm^{-1} and $O_{zeolite} \rightarrow Cu(II)$ charge transfer (CT) transitions at 34 000 cm^{-1}, the $O_{bridge} \rightarrow Cu$ CT transition in the Cu_2O_2 moiety of **A** at 22 700 cm^{-1} can be observed. A major decrease of the 22 700 cm^{-1} band intensity is observed after 1.5 min in He at 500 °C. This is followed by a minor decrease while no further changes can be discerned after 10 min. At this stage, the spectrum is also characterized by a background at about 19 000 cm^{-1}. Upon switching to an O_2 flow at 500 °C (Fig. 1(b)) the 22 700 cm^{-1} band was completely reinstalled after about 1.5 min. These data show that, at 500 °C, the O_2 desorption from and O_2 incorporation in the **A** core proceed at about the same rate. These two experiments corroborate that the species connected with the 22 700 cm^{-1} band involves extra-lattice oxygen that is easily desorbed in He at 500 °C and is quickly reinstalled in O_2. At lower temperatures however, this

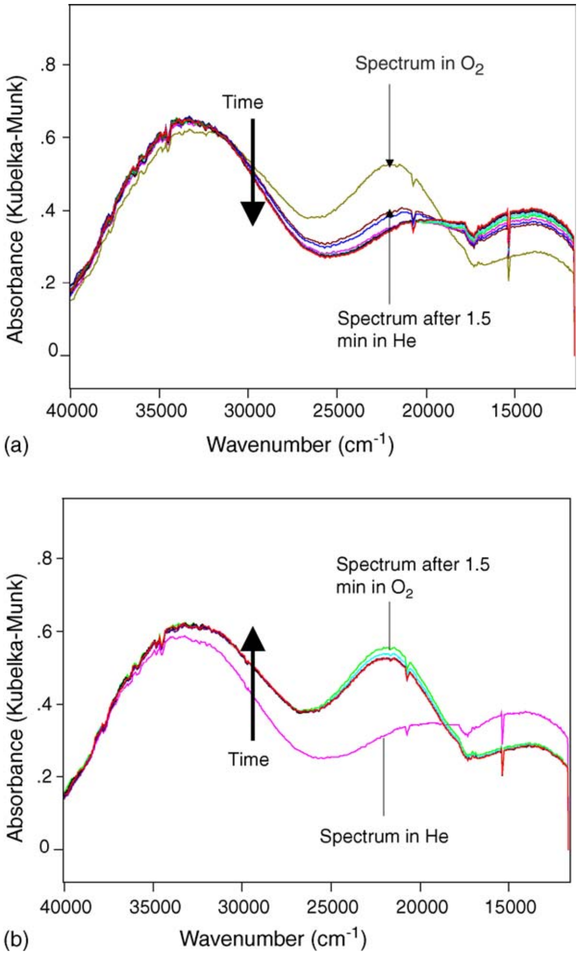

Fig. 1. Fiber-optic UV–vis spectra of CZ-12-0.54 during a O_2–He switch (a) and He–O_2 switch (b) at 500 °C. The time interval between two spectra is 1.5 min. The arrow represents the time evolution.

extra lattice oxygen species is stable in He. When a O_2 calcined CZ-12-0.54 sample was heated in He from RT to 500 °C, a sharp intensity decrease of the 22 700 cm^{-1} band was observed at about 370 °C, caused by the release of O_2 from the bis(μ-oxo)dicopper core. The subsequent calcination of this sample (after treating in He at 500 °C and cooling to RT) resulted in the formation of the **A** core starting at a temperature of about 280 °C. Comparing this result with the calcination of a hydrated sample (see also next paragraph), it is seen that for this dehydrated sample the formation temperature of the **A** core is about 70 °C lower. This is interesting from the point of view of selective oxidation catalysis. In order to avoid deep oxidation of the substrate, it is often preferred to operate at low temperatures and thus this highly active **A** core starts forming at about 280 °C.

Fig. 2 shows the spectra taken upon the interaction of the calcined CZ-12-0.54 sample with methane from RT to 225 °C, at a heating rate of 10 °C min^{-1}. Comparing this result with the results obtained during heating in He (as presented above), it is clear that methane causes a full disappearance of the 22 700 cm^{-1} band already at much lower temperature. Previously, it was found that the decay of the 22 700 cm^{-1} band when interacting with methane obeys a first-order reaction with half-lives of about 4 min, 35 and 9 s at 125, 175 and 225 °C, respectively [9].

3.2. Calcination in O_2 at different temperatures

Several research groups have shown that high-temperature calcination (at 600 or 700 °C) is favorable for the formation of α-oxygen, the species responsible for methane–methanol and benzene–phenol conversion in Fe-ZSM-5 [10,11]. Therefore, we studied the influence of the calcination temperature on the formation of the **A** core for the CZ-12-0.54 sample. Fig. 3 compares the UV–vis–NIR spectra collected after overnight calcination at temperatures ranging from 250 °C up to 750 °C with a 50 °C interval. A temperature of about 350 °C is needed to form the copper species responsible for the 22 700 cm^{-1} band. The maximum intensity of this band was reached after calcination at 650 °C and almost no intensity was left after calcination at 750 °C. These results clearly indicate that there is an optimal calcination temperature region between 450 and 650 °C when starting from a hydrated sample. Fig. 4 also shows that calcination at 450 °C, after calcination at 750 °C, results in a much lower intensity of the 22 700 cm^{-1} band compared to the first calcination at 450 °C. Thus, it can be concluded that the treatment at 750 °C leads to the irreversible loss of the capability to stabilize the **A** core in the ZSM-5 structure. From Fig. 3, it is also clear that the 22 700 cm^{-1} band is accompanied by the formation of a NIR band at 6200 cm^{-1}, which has not been assigned yet. The main reason for this is the lack of NIR spectra for the bis(μ-oxo)dicopper model complexes. However, from the data obtained so far it is evident that this band is related to the formation of the **A** core as can be seen from the spectra of (i) the Cu-ZSM-5 series with increasing Cu loading

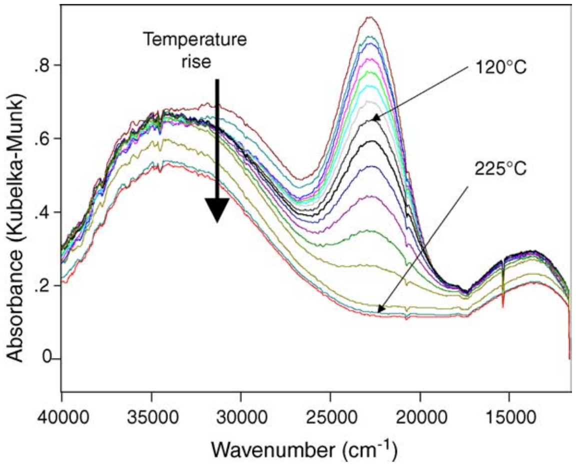

Fig. 2. Fiber-optic UV–vis spectra of a calcined CZ-12-0.54 sample during reaction with CH_4 at a heating rate of 10 °C/min from RT up to 225 °C. The time interval between two spectra is 1.5 min or a temperature difference of 15 °C. The arrow represents the temperature evolution.

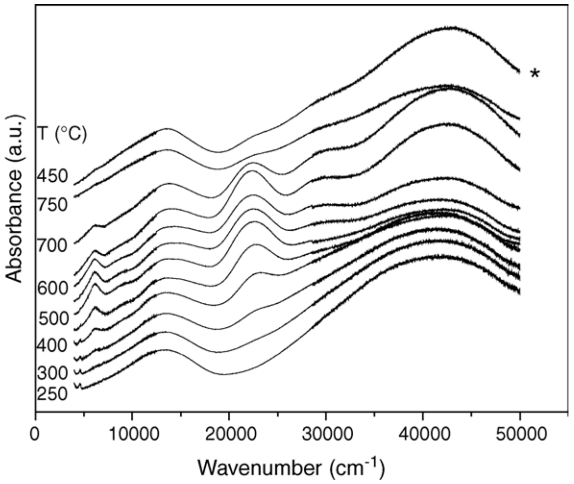

Fig. 3. DRS spectra of the CZ-12-0.54 sample taken at RT after calcination in O_2 at different temperatures ranging from 250 °C up to 750 °C. The temperature difference between two spectra is 50 °C. The spectrum marked with asterisk (*) is the DRS spectrum of CZ-12-0.54 calcined at 450 °C after calcination at 750 °C.

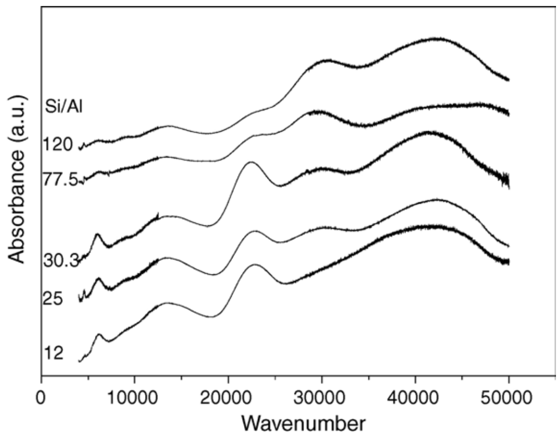

Fig. 4. DRS spectra at RT of a Cu-ZSM-5 series with increasing Si/Al ratio (CZ-12-0.54, CZ-25-0.51, CZ-30.3-0.47, CZ-77.5-0.55 and CZ-120-0.88) after calcination in O_2 at 450 °C.

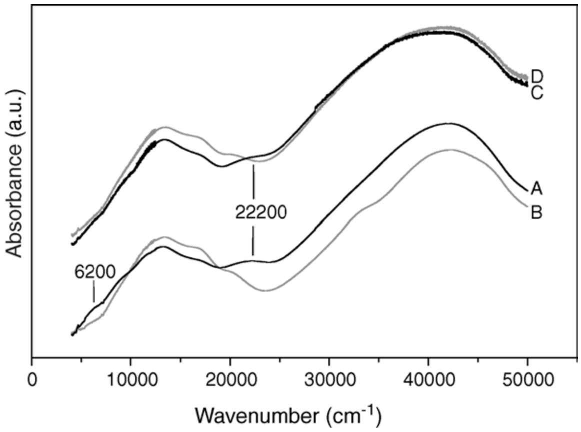

Fig. 5. DRS spectra at RT of the Cu-MOR samples CM-8.8-0.50 (A: after calcination and B: after reaction with methane) and CM-5.3-0.39 (C: after calcination and D: after reaction with methane).

[9] and (ii) Cu-ZSM-5 after reaction with methane showing that also the 6200 cm^{-1} band has disappeared together with the 22 700 cm^{-1} band (also for Cu-MOR, see Fig. 5). However, there is also one counter-argument to assign the 22 700 and 6200 cm^{-1} bands to the same species, i.e. their temperature of maximal intensity do not coincide. While the 22 700 cm^{-1} band gains maximal intensity after calcination at 650 °C, the 6200 cm^{-1} band is most intense in the 500–600 °C temperature range.

When the CZ-12-0.54 sample (calcined at 450 °C) was extracted after reaction with methane at 200 °C, 8.1 μmol methanol/g zeolite was found, compared to 0.7 μmol methanol/g for the sample calcined at 750 °C, confirming our prediction based on the spectra above. As a result, it can be concluded that calcination at temperatures higher than 700 °C leads to an irreversible loss of the formation of the bis(μ-oxo)dicopper core and the related capability to convert methane into methanol.

3.3. Influence of the Si/Al ratio

As was mentioned in our previous work, the 22 700 cm^{-1} band is only found for the highly loaded Cu-ZSM-5 samples, i.e. with Cu/Al ratio >0.2 [5,6,9]. This observation lead to the interpretation that at low loadings, the Cu^{2+} ions occupy sites with two Al ions in close proximity, leading to Cu^{2+} coordinations involving lattice oxygen only after dehydration. These Cu^{2+} coordinations correspond to the $g_{||}$-signals of 2.33 and 2.27 in EPR [12]. At higher Cu^{2+} loadings, also the sites with one Al atom are exchanged and extra lattice anionic ligands like OH$^-$ and acetate anions (form the Cu-acetate salt) fulfil the charge compensation requirements. Our findings indicate that during calcination, these extra lattice ligands are replaced by molecular O_2 bridging two closely located Cu atoms. In zeolites with low Si/Al ratios, the amount of isolated Al atoms is relatively small compared to the zeolites with higher Si/Al ratios. Thus, after calcination of these Cu^{2+} exchanged zeolites with higher Al contents, the **A** core formation is expected to be less pronounced. On the other hand, when Al contents are further reduced, the presence of isolated Al atoms is more likely to occur, but the isolated Al might be too far apart making it impossible for O-ligands to bridge two Cu atoms. Therefore an optimum in the Si/Al ratio is expected for the formation of the **A** core. This optimum is investigated in this section.

In Fig. 4, the UV–vis spectra of a series of calcined Cu-ZSM-5 samples with increasing Si/Al ratio ranging from 12 to 120, are given. They show that the **A** core is formed in all the Cu-ZSM-5 samples. The samples CZ-12-0.54, CZ-25-0.51 and CZ-30-0.47 have the most intense 22 700 cm^{-1} band while for the samples with higher Si/Al ratio (CZ-77.5-0.55 and CZ-120-0.88) the intensity of this band is drastically decreased. Thus, it can be concluded that the optimal Si/Al ratio for the stabilization of the **A** core is between 12 and 30 for ZSM-5. Testing these Cu-ZSM-5 samples in the reaction with methane resulted in the following methanol yields after extraction: 8.1 μmol/g for CZ-12-0.54 (4.3 wt.% Cu), 4.1 μmol/g for CZ-25-0.51 (2.0 wt.% Cu), 2.7 μmol/g for CZ-30-0.47 (1.5 wt.% Cu), 0.9 μmol/g for CZ-77.5-0.55 (0.68 wt.% Cu) and 0.66 μmol/g for CZ-120-0.88 (0.77 wt.% Cu). It can be seen that for the first three samples, with Si/Al ratio between 12 and 30, the ratio of methanol yield to Cu wt.% (Cu wt.% are given between brackets) is about the same, indicating that the fraction of active sites is comparable for the three samples. In contrast, the ratio of methanol yield to Cu wt.% for the two samples with highest Si/Al ratio is much lower, corroborating the UV–vis results, i.e. these samples contain a much lower fraction of active bis(μ-oxo)dicopper core. In conclusion, this optimum in the Si/Al ratio clearly indicates that the **A** core requires a specific Al distribution.

3.4. Influence of the zeolite topology

An extended series of zeolites with topologies of MOR, FER, EMT, BEA and FAU, were exchanged with high loadings of Cu^{2+} in order to study the stabilizing properties of the zeolites towards the **A** core. Out of all these samples, only for Cu-MOR an absorption band in the 22 000 cm^{-1} range was observed. Fig. 5 shows the UV–vis–NIR spectra of CM-8.8-0.5 and CM-5.3-0.39 after calcination and after reaction with methane. It is clear that a band at 22 200 cm^{-1}, and possibly also at 6200 cm^{-1} is formed (both less pronounced than in CZ-12-0.58), and disappears upon reaction with methane. Fig. 6 shows the UV–vis–NIR spectra of the calcined CE-4-0.36, CF-6.2-0.42, CB-9.8-0.5 and CY-2.7-0.45, and in none of the spectra a clear band at about 22 000 cm^{-1} can be discerned. Knowing that also the Si/Al ratio is an important factor, USY samples with Si/Al ratios of 13.5, 14.5, 27.5 and 36.9 were studied, but none of these were capable of bis(μ-oxo)dicopper core stabilization. Finally, also 10 silicas and aluminas were impregnated with Cu^{2+} and after calcination, no significant absorption in the region typical for the **A** core could be observed (spectra not shown).

In Fig. 7, the methanol extraction results obtained after reaction of the O_2-activated materials with methane are summarized. In order to estimate the reactivity with respect

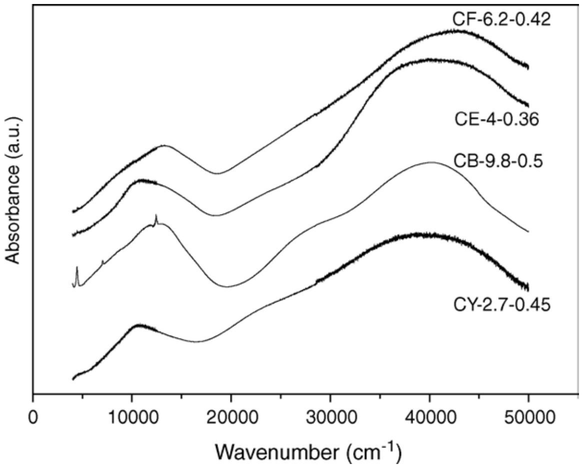

Fig. 6. DRS spectra collected at RT after overnight calcination in O_2 at 450 °C for the zeolite samples CF-6.2-0.42, CE-4-0.36, CB-9.8-0.5 and CY-2.7-0.45.

to Cu-ZSM-5, the data obtained for the Cu-ZSM-5 series with Si/Al ratio of 12 and increasing Cu loading, which we reported previously, [9] are added to the figure. The line fit through the data shows that above Cu/Al = 0.3 the methanol yield reaches a plateau. However, the intensity of the 22 700 cm^{-1} band still increases above Cu/Al = 0.3 [5,6,9]. This seeming contradiction is probably due to a hampered methanol extraction caused by pore blocking in the highly loaded Cu samples. This interpretation is corroborated by temperature programmed desorption experiments, giving the amount of desorbed CO_2, which is formed by the decomposition of the methanol at about 300 °C. More specifically, TPD showed that for the Cu/Al = 0.58 sample, a much higher amount of CO_2 (21.7 μmol/g, solid square in Fig. 7) was desorbed than the 8.2 μmol methanol/g that could be extracted. On the other hand, for the Cu/Al=0.31 sample, the amount of desorbed CO_2 is roughly equal to the amount of extracted methanol (6.7 and 8.9 μmol/g, respectively). Assuming a Cu:CH_3OH stoichiometry of 2:1 one can calculate that 4.6% of the Cu atoms in the CZ-12-0.31 sample participate in this stoichiometric conversion of methane into methanol. Before making the comparison with the other Cu materials, it needs to be stressed that the extraction method has to be seen as a rather rough analysis method. While the TPD results above show that only 38% of the methanol is extracted from the highly Cu-loaded ZSM-5 samples, it is hard to predict whether a similar fraction of unextractable methanol can be expected for other zeolite topologies or not, what results in a very large error margin on this method.

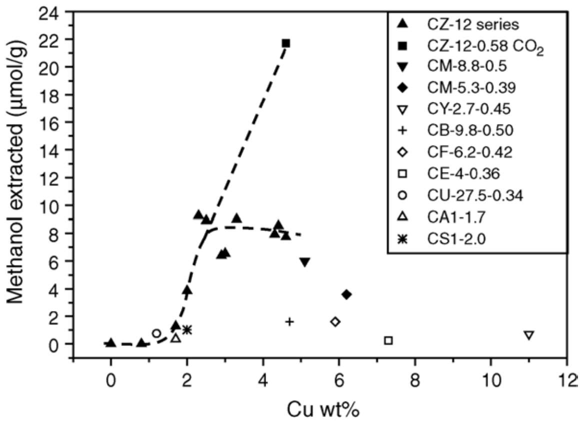

Fig. 7. Amount of methanol extracted/g of Cu-sample, as a function of the Cu wt.% of the sample. For the CZ-12 series, CY-2.7-0.45, CE-4-0.36, CU-27.5-0.34, CA1-1.7, CS1-2.0 the methanol yields after reaction with methane at 200 °C are given, for CM-8.8-0.50, CM-5.3-0.39, CB-9.8-0.50 and CF-6.2-0.42 the yields after reaction at 150 °C are displayed.

Fig. 7 shows very low methanol yields, i.e. below 1 μmol/g, for CE-4-0.36, CY-2.7-0.45, CU-27.5-0.34, CS1-2.0 and CA1-1.7. These extraction data confirm the trend expected from the UV–vis–NIR data, where a band at around 22 000 cm^{-1} was absent.

In the case of CF-6.2-0.42 and CB-9.8-0.50, an interesting result is obtained: after reaction with methane at 200 °C a large amount of methanol was extracted (12 and 4.2 μmol/g, respectively). Based on the in-situ UV–vis–NIR spectra, one would not expect such high methanol yields for these two zeolites as no band around 22 000 cm^{-1} could be seen. However, when the reaction temperature was lowered to 150 °C, the methanol yield dropped to 1.6 μmol/g zeolite (results after reaction at 150 °C shown in Fig. 7) for both zeolites whereas the methanol yield of CZ-12-0.58 is equal to 8.2 μmol/g for both temperatures. The present results indicate that in the case of CF-6.2-0.42 and CB-9.8-0.50, an activated copper-oxygen species, other than bis(μ-oxo)dicopper, is present that is capable of oxidizing methane into methanol at temperatures of about 200 °C but not at 150 °C, whereas the **A** core is already active at 125 °C. For the two mordenite samples, which also displayed the bis(μ-oxo)dicopper band, i.e. CM-8.8-0.50 and CM-5.3-0.39, a methanol yield after reaction at 150 °C is obtained that is comparable with the methanol yields obtained for the Cu-ZSM-5 series (6.0 and 3.6 μmol/g, respectively as displayed in Fig. 7). However, if the intensity of the band at 22 000 cm^{-1} of the calcined CM-8.8-0.50 and CM-5.3-0.39 (Fig. 5) is compared with the Cu-ZSM-5 series [9], a larger yield of methanol with respect to the band intensity is found in the former case. The presence of large 12-ring pores in mordenite might explain the increased extracted methanol yield in comparison with Cu-ZSM-5 containing only 10-ring pores. This result could be very important when selective oxidation catalysis with these Cu materials comes into play as fast desorption of the products is necessary in order to avoid deep oxidation. When the reaction temperature was increased to 200 °C, the methanol yield was almost tripled (16 and 13 μmol/g for CM-8.8-0.50 and CM-5.3-0.39, respectively). This may indicate that also in the MOR samples, two active copper-oxygen species are present and at low temperatures (150 °C), only the **A** cores contribute in the methane oxidation reaction, whereas at higher temperatures (200 °C), both species are active resulting in the high methanol yields. The nature of these other copper sites requires further investigation.

3.5. Comparison with Fe-ZSM-5

A number of similarities with the Fe-ZSM-5 system, active in methane to methanol and benzene to phenol oxidation, as first reported by Panov and co-workers [13–15], can be remarked. Also in the Fe system, methanol did not desorb but rather decomposed at higher temperature and was only detected after extraction. In this way, the highest amount of extracted methanol reported is equal to 14 μmol/g, which is in the same order of magnitude as the values obtained for Cu-ZSM-5. It is also interesting to draw the attention on similar problems of extraction and pore blocking, encountered in the quantitative analysis. First, Panov et al. showed that each extraction is incomplete in the sense that about 30% of methanol is unextractable. Second, they found that for the concerning samples with lowest amounts of active oxygen species, 100% of the O-species participate in the methane oxidation, while for the samples with the highest concentration of active sites, only 50% of these sites participate in the reaction, due to pore blocking. Thus, while Panov et al. report that the problem of pore blocking inhibits half of the sites to react with methanol, we believe that all bis(μ-oxo)dicopper sites do react (as the 22 700 cm^{-1} band completely vanishes), but that pore blocking is a problem at the point of extraction, i.e. only 38% of methanol is extracted for the Cu/Al = 0.58 sample. From the point of view of application, a first important difference between Fe-ZSM-5 and Cu-ZSM-5 is that for Fe-ZSM-5 the active species, called α-oxygen, can only be produced by N_2O while for Cu-ZSM-5, also O_2 is effective. Second, the typical absorption band at 22 700 cm^{-1} for Cu-ZSM-5 is an easy way to study and thus optimize the samples.

As Panov et al. reported, Fe-ZSM-5 is also capable of hydroxylating benzene into phenol using N_2O. Unlike the oxidation of methane, the reaction product, phenol, could be desorbed without extraction in a liquid phase, making it possible to perform this reaction in a continuous way. As there are already a number of similarities found between Cu-ZSM-5 and Fe-ZSM-5 in the oxidation of methane, it might be worthwhile investigating the activity and desorption behavior of Cu-ZSM-5 and other Cu based zeolites in the reaction with benzene. The present study is an important fundamental step forward for the further investigations regarding selective gas phase oxidation of methane and benzene using Cu based zeolites as catalysts.

4. Conclusions

In this work, the stabilization of the **A** core was investigated in zeolites, silicas and aluminas. The study of 12 Cu zeolites, other than Cu-ZSM-5, and 10 Cu silicas and aluminas showed that specific conditions of zeolite topology and Al distribution must be fulfilled in order to stabilize the **A** core: only ZSM-5 and MOR can do it. The stabilization of this Cu_2O_2 core requires calcination in O_2 at a temperature of at least 280 °C and not higher than 700 °C. For ZSM-5, the optimal Si/Al ratio is situated between 12 and 30.

The interest in this **A** core originates from the key role it plays in both the catalytic NO decomposition and the selective methane oxidation into methanol. For the latter reaction, additional evidence for the assignment of the **A** core as active site was found: (i) after calcination at 750 °C in O_2, CZ-12-0.58 irreversibly looses its capacity of stabilizing the **A** core and as a result the methanol yield after this high temperature calcination dropped significantly, (ii) not every Cu-ZSM-5 sample is capable of hydroxylating methane into methanol to a significant extent: only the Cu-ZSM-5 samples with a Si/Al ratio between 12 and 30, who possesses an intense CT band around 22 000 cm^{-1} after calcination in O_2, are capable of producing methanol in significant amounts, and (iii) only in the zeolites ZSM-5 and MOR, which possess the **A** core, significant activity towards the methane oxidation was found at low temperatures (150 °C). Cu-FER and Cu-BEA were only active at higher temperatures (200 °C), suggesting that another yet to be identified Cu site is active.

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