CO interaction with Cu(I)-MCM-22 zeolite: density functional theory investigation

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ABSTRACT

MCM-22 zeolite has been widely used in many applications for catalysis and adsorption. Especially, this material exchanged with Cu^+ *cation (Cu(I)-MCM-22) is an active catalyst in green chemical reaction, such as decomposition of NO and* N_2O*. The local geometry of* Cu^+ *in vicinity of Al (III) replacement in six different Si (IV) sites and CO interaction with the most stable* Cu^+ *in each Al site were explored using periodic density functional theory (DFT) method. The CO stretching frequencies were computed applying the* ω/r *scaling method in which frequencies were determined at high quantum level (couple cluster) and CO bond length calculated at DFT level. The results showed that* Cu^+ *cation located in the channel wall position and intersection position coordinated with 3 or 2 framework oxygen atoms, respectively, before CO adsorption and* Cu^+ *cation coordinated with 2 framework oxygen atoms after CO adsorption. The interaction energies between CO and* Cu^+ *cation were in range -148 to -195 kJ.mol*$^{-1}$ *and CO frequencies exhibit two peaks at 2151 and 2159 cm*$^{-1}$ *in good agreement with experimental data. This investigation brought us to understand the* Cu^+ *location in MCM-22 and CO adsorption in Cu(I)-MCM-22 zeolite.*

Keywords: *DFT, CO probe, MCM-22 zeolite, CO frequencies,* Cu^+ *cation.*

INTRODUCTION

MCM-22 (MWW topology structure in IZA code) has shown interesting structure with large and medium pore size including 12-MR large supercage (7.1 x 7.1 x 18.2Å) connected with 10-MR crossing window (4.0 x 5.4Å) and 10-MR sinusoidal channels (4.0 x 5.9Å) located in the intralayer space of MCM-22 [1]. This material with metal or alkali ion exchange has been used in many applications for catalysis, adsorption [2-6]. Among of exchange ions in MCM-22, Cu^+ cation exchange in MCM-22 zeolite (Cu(I)-MCM-22) is promising for catalytic reaction in NO, N_2O decomposition process into N_2 and O_2 [7].Although Cu(I)-MCM-22 showed disadvantage such as: low reactivity, it illustrated promising material for NO or N_2O decomposition process because of maintaining reactivity for long time steaming. A number of studies showed that the Cu^+ cation position in extra-framework zeolite is an important factor of NO and N_2O decomposition [8-10]. Therefore, characterization of Cu^+ cation location and their coordinates with framework oxygen atoms are crucial for understanding of catalytic activitiesand adsorption properties in copper exchanged zeolite morphology.

In the experiment, the CO molecular was used as good probe in many cation extra-framework zeolites by various means, such as: FTIR, UV-vis, XANES, and EXAFS spectroscopy [10-13]. These techniques brought indirect evidence about the Cu^+ cation existence in different positions depending on the zeolite structure, Si/Al ratio, number of framework oxygen atoms coordination and copper ion content. However, it could not afford a complete understand of Cu^+ cation location and its activity at the atomic scale level. Earlier studies [9, 14] reported that Cu^+ cation located in the main or zig-zag channels in vicinity of Al atom site and coordinated with two, three, or four framework oxygen atoms [11].

Cu^+ cation location and its interaction with CO were also computationally investigated in various zeolite structures (Cu(I)-ZSM-5, Cu(I)-MFI, Cu(I)-FER) by mean of combined QM-pot and periodic DFT [14-18]. These results showed that two type of Cu^+ position were found: (i) type I, Cu^+ cation located on the wall channel surface coordinated with 3 or 4 framework oxygen atoms; (ii) type II, Cu^+ cation located on the intersection site formed between the main and the zig zag channel. It showed that Cu^+ cation behaved different adsorption energies and frequencies in different sites. The CO adsorption energies (approximately 40 kcal) and frequencies (2159 cm^{-1}) are the highest corresponding to Cu^+ located in the intersection site (type II sites) of MFI, FER, ZSM-5 zeolites.Up to now, there are several studies about Cu(I)-zeolite and the experimental data of Cu(I)-MCM-22 zeolite can explain their results based on the knowledge of these zeolite structures.

The aim of this contribution was to carry out the investigation of the possible Cu^+ cation location on each of the vicinity of AlO_4 tetrahedron in MCM-22 and to compute the CO adsorption on the most stable Cu^+ cation site in each AlO_4 tetrahedron using periodic density functional theory. ω/r method was used to evaluate CO frequencies and compared to the experiment. This bronght us completely understand experimental data of Cu(I)-MCM-22 at the atomic scale.

MODEL AND METHOD

The MCM-22 framework has a hexagonal unit cell with P6/mmm space group ($T_{72}O_{144}$, where T is either a Si or Al atom) having eight inequivalent T sites and thirteen inequivalent framework oxygen atoms. The MCM-22 structure and the numbering scheme following ref. [19] and the positions of Cu^+ cation to balance the charge when Al substitute Si site are shown in Figure 1. Calculations were performed with the unit cell (UC) parameters obtained from Database of Zeolite Structure [1]. All calculations were carried out with one framework Al atom and charge-compensating Cu^+ cation in UC, that corresponded to Si/Al ratio of 71; Al was substituted to six of eight inequivalent T sites and all possible Cu^+ cation positions in vicinity of AlO_4 tetrahedrons were considered. In order to avoid the collapsion of the framework structure, Al in T6 is not considered and neither Al in T7 neither these sitesare located in the pocket of MCM-22 which cannot be accessible for probe molecules.

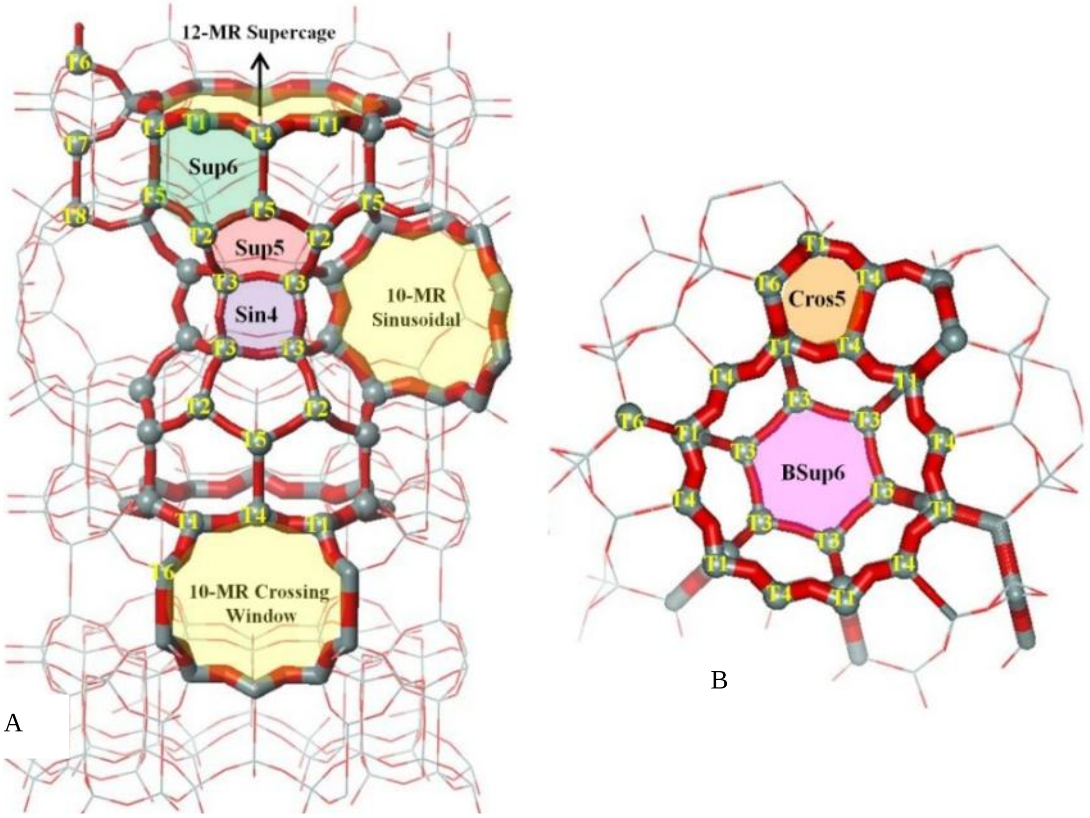

Figure 1. Structure of MCM-22 framework, numbering scheme and Cu^+ cation positions, (A) view from *a* or *b* direction; (B) view from *c* direction

All calculations were performed with the periodic model using the VASP-5.3.3 program package[20,21]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[22,23]projector augmented the wave approximation (PAW) [24, 25], and the plane the wave basis set with a kinetic energy cut-off of 400 eV was used; the Brilloun-zone sampling was restricted to the Γ-point. Geometry optimizations were performed with fixed UC volume and shape while relaxing positions of all atoms. Zero-point energies (ΔZPE) were calculated within the harmonic approximation considering 6 degrees of freedom for CO. Two displacement steps in each direction with a step size of 0.005 Å were used to calculate numerically the second derivatives. Following the strategy used previously for CO interaction with Cu(I)-zeolite [18] adsorption energy was expressed as the following equation:

$$\Delta E_{ads} = E_{(CO\ldots Cu(I)\text{-}MCM\text{-}22)} - E_{CO} - E_{(Cu(I)\text{-}MCM\text{-}22)} + \Delta ZPE$$

The stretching frequencies of CO adsorbed on Cu^+ cation sites were evaluated using ω_{CO}/r_{CO} scaling method (detail in ref. [26]). Briefly, The bond length (r_{CO}) and harmonic frequencies of CO (ω_{CO}) were calculated at DFT and (CCSD(T)) levels, respectively, from the set of small cluster (Cu^+CO, $H_2O\ldots Cu^+CO$, $(H_2O)_2\ldots Cu^+CO$, $F^-\ldots Cu^+CO$, and $F^-\ldots Cu^+CO$, and $(F^-)_2\ldots Cu^+CO$) using G09 program. The linear relationship between stretching frequencies at CCSD(T) level and r_{CO} at DFT level accompanying with the correction of harmonic and aharmonic frequencies interpolated exactly with frequencies of CO from CO adsorption complexes with Cu(I)-MCM-22 at DFT level.

RESULTS

Cu^+ cation location

Table 1. The distances of Cu^+ cation with framework oxygen atoms (in Å) of optimal geometries on all possible charge-exchange positions and relative energies (E_{rel}) (in $kJ.mol^{-1}$) compared with the most stable site in each T site.

Al Site	Cu^+ position	$r(Cu^+-O_f)$	E_{rel}
T1	Sup6	1.962 1.994 2.503	0.0
	Cro5	1.913 1.983 2.583	9.9
	Inter	2.006 2.011	28.4
T2	Sup6	1.949 1.955 2.298	0.0
	Sin5	1.994 2.031 2.096	15.9
	Sup5	1.913 1.946 2.574	18.8
T3	Bsup6	1.947 1.981 2.332	0.0
	Sup5	1.898 1.987 2.573	49.7
	Inter	1.973 2.099 2.371	53.2
	Sin5	1.972 2.013 2.065	62.5
	Sin4	1.962 2.049	87.5
T4	Sup6	1.970 1.992 2.459	0.0
	Cro5	1.920 1.974 2.532	3.4
	Inter	2.000 2.002	15.7
T5	Sup6	1.911 1.926 2.396	0.0
	Sup5	1.972 2.053 2.057	12.8
	Sin5	1.907 1.973 2.530	19.5
T8	Sin5	2.004 2.071 2.071	0.0

Cu^+ cation could be located on several positions to compensate the charge in vicinity of Al atom site. All the Cu^+ cation positions and relative energies of these positions are presented in Table 1.The T sites and Cu^+ cation possible charge-exchange positions are shown in Figure1. The symbols of the Cu^+ cation location in Table 1 and Figure 1 was explained as the following. Sup6 (light green color in Figure 1A) means 6-membered ring located on the supercage and Al can occupy at T1, T2, T4, and T5 in this ring. Sup5 (light pink color in Figure 1A) means 5-membered ring located on the supercage and Al can occupy at T2, T3 and T5 in this ring. Sin5 denoted 5-membered ring located on the walls of the sinusoidal channels and Al in this ring can place at T2, T3, T5, and T8. Sin4 (purple color in Figure 1A) denoted 4-membered ring located on the walls of the sinusoidal channels and Al in this ring was positioned only at T3. Cros5 (light organge color in Figure 1B) denoted 5-membered ring located on crossing window channel corresponding to Al atoms occupy at T1, T4 and T6. Inter sites are located at the intersection of the supercage and crossing window or the edge of sinusoidal channels, Al can be located in T1 and T3 in this site. Bsup6 (light purple color in Figure 1B) means 6-membered ring located on bottom of the supercage and involve only Al in T3. From the results of Table 1, Cu^+ cation coordinated with 2 or 3 framework zeolite oxygen atoms and the distances of Cu^+ cation and framework oxygen atoms (Cu^+-O_f) lower than 2.6 Å are exhibited. The position of Cu^+ cation can be classified into two types following previous studies [15, 17]: (i) type I located on channel wall of zeolite framework, five- memberedring (Sin5, Cros5) or six-membered ring (Sup6, Bsup6), coordinated with 3 framework oxygen atoms and (ii) type II located in the intersection coordinated with only 2 framework oxygen atoms (Inter). Comparison of energies of optimal geometries (E_{rel}) in each Al site, it is clear that the most stable Cu^+ cation positions are located on the six-membered ring of supercage (Figure 2A) involve Al atom in T1, T2, T4, and T5 and the two other positions are occupied on Bsup6 (Figure 2C) and Sin5 ring (Figure 2E) which Al atom is in T3 and T8, respectively. However, upon CO adsorption the Cu^+ cation coordinates with framework oxygen atoms change from 3 to 2 and form plane with O-Al-O (Table 2 and Figure 2B, 2D, 2F).

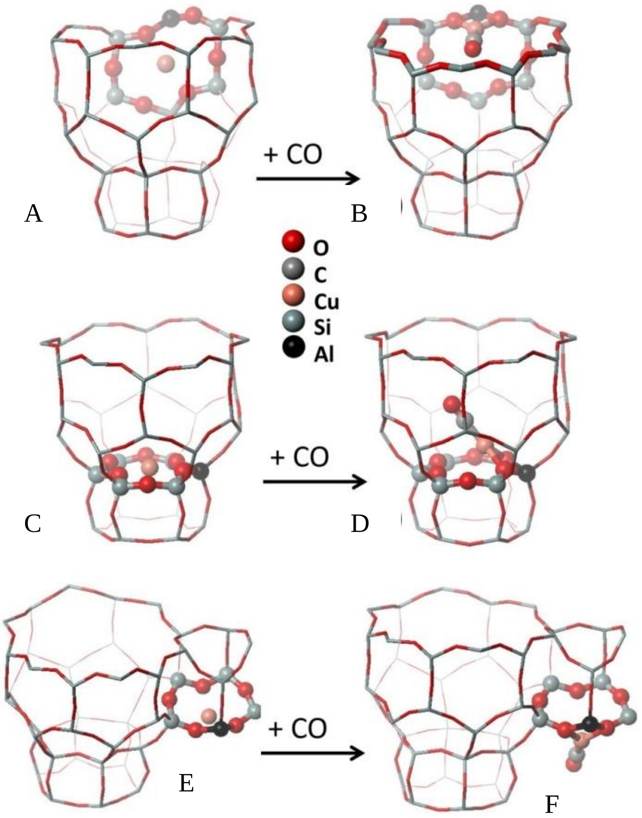

Figure 2. Cu^+ cation positions and CO adsorption complexes on MCM-22 zeolite shown for Al in T1 (A, B), T3(C, D) and T8 (E, F), respectively

CO interaction with Cu^+ cation

Table 2. Parameters of CO interaction with the most stable Cu^+ cation in each Al site, distances of Cu^+ with framework oxygen atoms in Å, interaction energies (E_{int})in $kJ.mol^{-1}$ and stretching frequencies (ν_{CO}) in cm^{-1}

Al site	Cu^+ position	$r(Cu^+\text{-}O_f)^a$	$r(Cu^+\text{-}O_f)+CO^b$	E_{int}	ν_{CO}
T1	Sup6	1.962 1.994 2.503	2.021 2.029	-176.23	2159
T2	Sup6	1.949 1.955 2.298	2.018,2.058	-148.83	2161
T3	Bsup6	1.947 1.981 2.332	1.995 2.049	-195.11	2152
T4	Sup6	1.970 1.992 2.459	2.048 2.051	-165.23	2159
T5	Sup6	1.911 1.926 2.396	2.022 2.039	-157.57	2158
T8	Sin5b	2.004 2.071 2.071	2.016 2.018	-184.06	2151

[a, b]: the number of coordinates and distances of Cu^+ cation with framework oxygen atoms before and after CO interaction, respectively.

The CO molecular has been used in many previous studies because it is sensitive and site-specific probe [13,26-29]. Therefore CO molecular is a suitable probe for Cu(I)-MCM-22 in this study.

From the results, CO interaction with Cu^+ cation would change Cu^+ cation coordinates and zeolite structure. Firstly, the number of coordinates of Cu^+ cation with framework oxygen atoms change from 3 (before CO interaction) to 2 (after CO interaction) and distances between Cu^+ cation and framework oxygen atoms are slightly prolong (Table 1). This is in good agreement with previous study [18]. However, compared with elsewhere [26,30], these results show that all Cu^+ cation positions change from type I position to type II position after CO interaction. Secondly, in order to understand the effect of Cu^+ cation coordinates change to zeolite structure, the deformation energies were calculated as the difference between Cu(I)-MCM-22 optimization and Cu(I)-MCM-22 obtained from optimal CO adsorption complexes. As the results from the Table 3, the deformation energies (E_{def}) contribute significantly and vary to different Al sites and Cu^+ cation positions ranging from 29.53 to 64.73 $kJ.mol^{-1}$. The CO interaction energies lie in range from -149 to -195 $kJ.mol^{-1}$ for the most stable Cu^+ cation sites of each Al position (Table 2). The interaction energies are different even Cu^+ cation located on the same charge-exchange position (Sup6) with different Al sites (T1, T2, T4, and T5).

Table 3. Deformation energies of the most stable Cu^+ cation position in each AlO_4 tetrahedron in $kJ.mol^{-1}$

Al site	Cu^+ position	E_{def}
T1	Sup6	34.92
T2	Sup6	55.40
T3	Bsup6	64.73
T4	Sup6	39.88
T5	Sup6	50.38
T8	Sin5b	29.53

The stretching frequencies of CO adsorption complexes in the most stable Cu^+ cation position are shown in Table 2 (ν_{CO}). Two bands of frequencies are observed: (i) 2158-2160 cm^{-1} involve Al in T1, T2, T4, T5 and (ii) 2151-2152 cm^{-1} corresponding to Al in T3 and T8, in good agreement with experimental data [13], within monolayer coverage.The frequencies are 2159 cm^{-1}, corresponding to all CO interact with Cu^+ cation located on six-membered ring of supercage and the other one are Cu^+ cation located on Sin5 or Bsup6 when Al is in T8 or T3, respectively in which CO frequency exhibited 2151 cm^{-1}.

DISCUSSION

DFT method describe exactly Cu^+ cation locations and stretching frequencies of CO adsorption complexes in Cu(I) zeolite. The present study shows similar results of Cu^+ cation position to previous studies [18,30,31] from cluster to periodic model. The Cu^+ cation position located in MCM-22 either on the top of channel wall ring (5 or 6-membered ring) and coordinated with 3 framework oxygen atoms (type I) or on the intersection forming between supercage (12-membered ring) and crossing window cage (10-membered ring) (type II) or edge of sinusoidal channel and coordinated with only two framework oxygen atoms. Compared to those in FER [26], ZSM-5 zeolite [30], Cu^+ cation located in this material do not coordinate with more than 3 framework oxygen atoms and the most stable Cu^+ cation position are on the 6-membered ring of the supercage. There is an exception Al in T8 (Table 1), Cu^+ cation occupied preferably on 5-membered ring of sinusoidal channel (Sin5). However, it is in good agreement with elsewhere [26, 27, 30, 32], Cu^+ cation coordinated with two oxygen atoms of AlO_4 tetrahedron after CO interaction. The interaction energies are higher than those earlier study as well as deformation energies (Table 3) due to change of ring morphology (Figure 3). The interaction energies are higher in this study than experimental data due to two reasons: (i) PBE method reported in earlier studies [18] overestimate about 96 kJ.mol^{-1}, (ii) the Si/Al ratio is lower in this work than in experiments (71 vs. 15) [30].

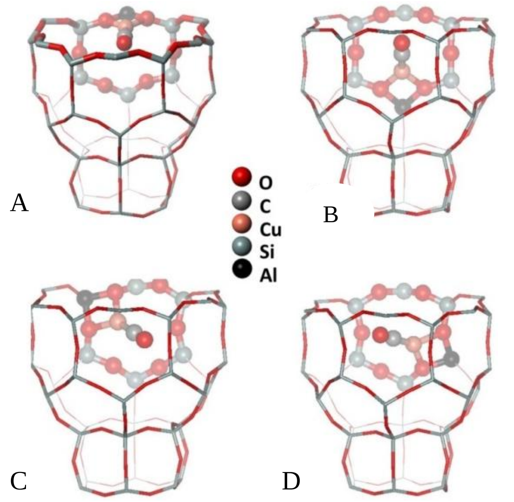

Figure 3. CO adsorption complexes on Sup6 ring of MCM-22 shown for Al in T1 (A), T2 (B), T4 (C), and T5 (D), respectively.

In order to understand Al site affect the CO interaction, considering CO interaction energies when Cu$^+$ cation occupy on the same Sup6 ring (Figure 3), the interaction energies are different as Al place in T1, T2, T4, and T5 . The lowest value is 148.83 kJ.mol^{-1} corresponding to Al in T2 and the highest is 176.23 kJ.mol^{-1} involve Al in T1 (Table 2). It can conclude that the interaction energies of CO with Cu$^+$ cation depend on not only the size and morphology of charge-exchange ring but also Al site. Comparing to those in FER [27], ZSM-5 [30], the reported adsorption energies are similar as CO interact with Cu$^+$ on the same ring morphology and independent with Al site. This is primary illustrate the Cu$^+$ cation position.Its activity depends on Al site rather than ring morphology. On the other hand, the stretching frequencies are independent to Al position (Table 2). It shows that there are two peaks of frequencies, the first one is about 2159 cm^{-1}dme to the Cu$^+$ cation located on Sup6 either Al in T1, T2, T4, or T5. The second one is about 2151 cm^{-1} as Al in T3 or T8 and Cu$^+$ cation located on Bsup6 or Sin5, respectively. The results in this study are very good agreement with experimental data (Figure 4) [13].

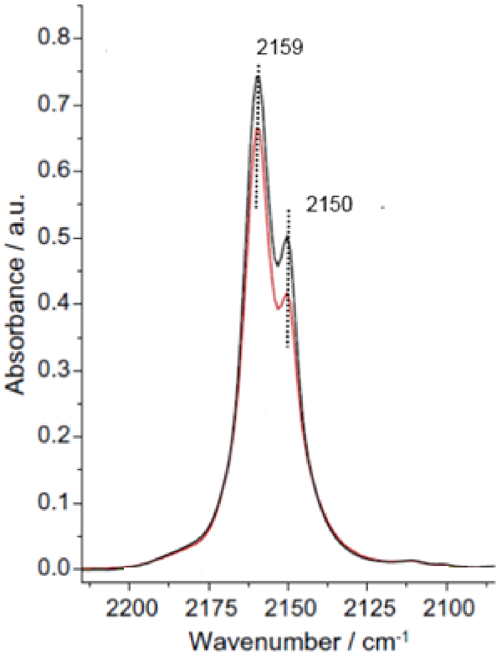

Figure 4. IR spectra of monolayer coverage of CO adsorption on Cu(I)-MCM-22 [13]

However, experimental data based on theoretical results of Cu(I)-ZSM-5 and FER zeolite explain that the peak at 2159 cm^{-1} due to Cu$^+$ cation adsorbed on intersection and the band 2150 cm^{-1} caused by partial charge result of the presence of two Al atoms in the ring. Therefore, this study evidences that experimental data of Cu(I)-MCM-22 cannot explain based on results of other zeolite.

CONCLUSION

The Cu(I)-MCM-22 and CO interaction with Cu$^+$ cation have been carried out using periodic density functional theory. The influences of the structure and Al sites to Cu$^+$ cation position were computationally explored. Cu$^+$ cation position

preferably located on the six-membered ring in supercage (Sup6) involved Al atom in T1, T2, T4, and T5), and in Bsup6 corresponding to Al atom in T3. Cu^+ cation coordinated with 3 framework oxygen atoms and change to 2 framework oxygen atoms after CO adsorption. The characterization of Cu^+ cation position depends on the Al site rather than charge-exchange ring. The CO adsorption energies of Cu^+ cation on Sup6 were shown in the range from 149 to 176 kJ.mol^{-1} and CO stretching frequencies are about 2159 cm^{-1}. On the other hand, CO adsorption energies of Cu^+cation on Bsup6 and Sin5 exhibited from 148 to 195 kJ.mol^{-1} and CO stretching frequencies are about 2151 cm^{-1}. This is in good agreement with experimental data of two peaks of stretching frequencies (2159 and 2150 cm^{-1}). The present study supports the evidence for the experiment to understand clearly about Cu(I)-MCM-22.

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Phản ứng của CO với zeolít Cu(I)-MCM-22: khảo sát lý thuyết phiếm hàm mật độ

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TÓM TẮT

Zeolít MCM-22 đã và đangđượcsử dụngrộngrãitrongnhiềuứngdụngđốivớixúctác và hấpphụ .Đặcbiệt, vậtliệunàyđượctraođổivới ion dương Cu^+ (Cu(I)-MCM-22) làmộtchấtxúctáchoạttínhđốivớicácphảnứnghóahọcxanh, chẳnghạnnhưsự phânlycủa N O và N_2O. Vị trí hìnhhọccụcbộ của ion Cu^+tạinhữngvùngxungquanh vị trí Al (III) khithaythế vớimỗi vị trí củasáu vị trí Si (IV) khácnhauvà phảnứngcủa CO đốivới Cu^+ổnđịnhnhấttạimỗi vị trí của Al đượckhảosátbằngphươngpháplý thuyếtphiếmhàmmậtđộ (DFT). Tầnsố daođộngcủa CO đượctínhtoánbằngphươngpháp tỷ lệ ω/rtrongđó tầnsố daođộngcủa CO (ω) đượcxácđịnhtạimứclượngtử cao (couple cluster) và chiềudài liênkết (r) đượctínhtoántạimức DFT . Kết quả tínhtoánchothấy ion dương Cu^+định vị tại vị trí trênthànhcủakhelỗ xốpvà vị trí giaonhaucủacáckhelỗ xốpđượckếthợpvới 3 và 2 nguyêntử oxy củacấutrúczeolít, theothứ tự lầnlượt, trướckhihấpphụ CO và ion dương Cu^+kếthợpvới 2 nguyêntử oxy củacấutrúczeolítsaukhihấpphụ CO . Nănglượngphảnứnggiữa CO và ion dương Cu^+nằmtrongkhoảngtừ -148 đến -195 kJ.mol^{-1}và tầnsố giaođộngcủa CO chỉ rahaiđỉnhtại 2151 và 2159 cm^{-1}và hoàntoànphù hợpvớikết quả thí nghiệm. Khảosátnàygiúpchochúng ta hiểuvề vị trí của ion dươngtrongzeolít MCM -22 và sự hấpphụ CO trongzeolít Cu(I)-MCM-22.

Từ khóa: *DFT, CO, zeolít MCM-22, tầnsố CO, ion dương Cu$^+$*

REFERENCES

[1]. http://www.iza-structure.org/databases/.

[2]. G.G. Juttu, R.F. Lobo, Characterization and catalytic properties of MCM-56 and MCM-22 zeolites. *Microporous and Mesoporous Materials*, 40, 9-23 (2000).

[3]. A.J.S. Mascarenhas, H.O. Pastore, H.M.C. Andrade, A. Frache, M. Cadoni, L. Marchese, Spectroscopic and catalytic studies on Cu-MCM-22: Effect of copper loading. *Impact of Zeolites and Other Porous Materials on the New Technologies at the Beginning of the New Millennium, Pts a and B,* 142, 343-350 (2002).

[4]. A. Frache, M. Cadoni, C. Bisio, L. Marchese, A.J.S. Mascarenhas, H.O. Pastore, NO and CO adsorption on over-exchanged Cu-MCM-22: A FTIR study. *Langmuir*, 18, 6875-6880 (2002).

[5]. J. Pawlesa, A. Zukal, J. Cejka, Synthesis and adsorption investigations of zeolites MCM-22 and MCM-49 modified by alkali metal cations. *Adsorption-Journal of the International Adsorption Society*, 13, 257-265 (2007).

[6]. P. Cicmanec, R. Bulanek, E. Frydova, M. Kolarova, Study of thermodynamic characteristics of CO adsorption on Li exchanged zeolites. *Adsorption-Journal of the International Adsorption Society*, 19, 381-389 (2013).

[7]. B.I. Palella, R. Pirone, G. Russo, A. Albuquerque, H.O. Pastore, M. Cadoni, A. Frache, L. Marchese, On the activity and hydrothermal stability of CuMCM-22 in the decomposition of nitrogen oxides: a comparison with CuZSM-5. *Catalysis Communications*, 5, 191-194 (2004).

[8]. B. Wichterlova, Z. Sobalik, J. Dedecek, Cu ion siting in high silica zeolites. Spectroscopy and redox properties. *Catalysis Today*, 38, 199-203 (1997).

[9]. R. Bulanek, P. Cicmanec, P. Knotek, D. Nachtigallova, P. Nachtigall, Localization of Cu+ sites and framework Al positions in high-silica zeolites: Combined experimental and theoretical study. *Physical Chemistry Chemical Physics*, 6, 2003-2007 (2004).

[10]. J. Dedecek, Z. Sobalik, Z. Tvaruzkova, D. Kaucky, B. Wichterlova, Coordination of Cu ions in high-silica zeolite matrices - Cu$^+$ photoluminescence, Ir of No adsorbed on Cu2$^+$, and Cu2$^+$ Esr Study. *Journal of Physical Chemistry*, 99, 16327-16337 (1995).

[11]. C. Lamberti, S. Bordiga, M. Salvalaggio, G. Spoto, A. Zecchina, F. Geobaldo, G. Vlaic, M. Bellatreccia, XAFS, IR, and UV-vis study of the Cu-I environment in Cu-I-ZSM-5. *Journal of Physical Chemistry B*, 101, 344-360 (1997).

[12]. C. Lamberti, S. Bordiga, A. Zecchina, M. Salvalaggio, F. Geobaldo, C.O. Arean, XANES, EXAFS and FTIR characterization of copper-exchanged mordenite. *Journal of the Chemical Society-Faraday Transactions*, 94, 1519-1525 (1998).

[13]. K. Frolich, R. Bulanek, E. Frydova, Interaction of CO probe molecules with Cu(+) in MCM-22 zeolite. *Microporous and Mesoporous Materials*, 186, 37-45 (2014).

[14]. D. Nachtigallova, P. Nachtigall, M. Sierka, J. Sauer, Coordination and siting of Cu+ ions in ZSM-5: A combined quantum mechanics interatomic potential function study. *Physical Chemistry Chemical Physics*, 1, 2019-2026 (1999).

[15]. D. Nachtigallova, P. Nachtigall, J. Sauer, Coordination of Cu+ and Cu2+ ions in ZSM-5 in the vicinity of two framework Al atoms. *Physical Chemistry Chemical Physics*, 3, 1552-1559 (2001).

[16]. P. Nachtigall, M. Davidova, D. Nachtigallova, Computational study of extraframework Cu+ sites in ferrierite: Structure, coordination, and photoluminescence spectra. *Journal of Physical Chemistry B*, 105, 3510-3517 (2001).

[17]. P. Nachtigall, O. Bludsky, D. Nachtigallova, P. Cicmanec, H. Drobna, R. Bulanek, Characterization of Cu(+) sites in FER: Combined computational and experimental TPD study. *Molecular Sieves: From Basic Research to Industrial Applications, Pts a and B*, 158, 925-932 (2005).

[18]. O. Bludsky, M. Silhan, P. Nachtigall, T. Bucko, L. Benco, J. Hafner, Theoretical investigation of CO interaction with copper sites in zeolites: Periodic DFT and hybrid quantum mechanical/interatomic potential function study. *Journal of Physical Chemistry B*, 109, 9631-9638 (2005).

[19]. C.O. Arean, M.R. Delgado, P. Nachtigall, H.V. Thang, M. Rubes, R. Bulanek, P. Chlubna-Eliasova, Measuring the Bronsted acid strength of zeolites - does it correlate with the O-H frequency shift probed by a weak base? *Phys Chem Chem Phys*, 16, 10129-10141 (2014).

[20]. G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys Rev B Condens Matter*, 49, 14251-14269 (1994).

[21]. G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science*, 6, 15-50 (1996).

[22]. J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. *Physical Review Letters,* 77, 3865-3868 (1996).

[23]. J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple (vol 77, pg 3865, 1996). *Physical Review Letters*, 78, 1396-1396 (1997).

[24]. P.E. Blochl, Projector augmented-wave method. *Physical Review B*, 50, 17953-17979 (1994).

[25]. G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B*, 59, 1758-1775 (1999).

[26]. O. Bludsky, M. Silhan, P. Nachtigall, T. Bucko, L. Benco, J. Hafner, Theoretical investigation of CO interaction with copper sites in zeolites: periodic DFT and hybrid quantum mechanical/interatomic potential function study. *J Phys Chem B*, 109, 9631-9638 (2005).

[27]. M. Davidova, D. Nachtigallova, R. Bulanek, P. Nachtigall, Characterization of the Cu+ sites in high-silica zeolites interacting with the CO molecule: Combined computational and experimental study. *Journal of Physical Chemistry B*, 107, 2327-2332 (2003).

[28]. O. Bludsky, M. Silhan, D. Nachtigallova, P. Nachtigall, Calculations of site-specific CO stretching frequencies for copper carbonyls with the "near spectroscopic accuracy": CO interaction with Cu+/MFI. *Journal of Physical Chemistry A*, 107, 10381-10388 (2003).

[29]. D. Nachtigallova, P. Nachtigall, O. Bludsky, Calculations of the site specific stretching frequencies of CO adsorbed on Li+/ZSM-5. *Physical Chemistry Chemical Physics*, 6, 5580-5587 (2004).

[30]. X.B. Zheng, Y.H. Zhang, A.T. Bell, Density functional theory study of CO adsorption on Cu(I)-ZSM-5. *Journal of Physical Chemistry C*, 111, 13442-13451 (2007).

[31]. R. Bulanek, K. Frolich, P. Cicmanec, D. Nachtigallova, A. Pulido, P. Nachtigall, Combined experimental and theoretical

investigations of heterogeneous dual cation sites in Cu,M-FER Zeolites. *Journal of Physical Chemistry C*, 115, 13312-13321 (2011).

[32]. R. Bulanek, H. Drobna, P. Nachtigall, M. Rubes, O. Bludsky, On the site-specificity of polycarbonyl complexes in Cu/zeolites: combined experimental and DFT study. *Phys Chem Chem Phys*, 8, 5535-5542 (2006).