Oxygen Isotope Exchange over Copper-Containing Mordenite: the Effect of Copper Loading and Si/Al Ratio

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Abstract

The oxygen isotope exchange over copper-containing mordenite with different copper loadings and Si/Al ratios was studied in temperature-programmed and isothermal regimes. The kinetics of the exchange was described quantitatively using a model comprising “fast” and “slow” sources of exchangeable oxygen atoms. The amount of the “fast” exchangeable oxygen in the materials is determined by the aluminum content, while the number of atoms belonging to the “slow” source is independent of the composition of the material and the experimental conditions. Copper-containing mordenites with a Si/Al ratio 6 containing dimeric species demonstrated measurable isotope exchange at 793-893 K. The decrease in the copper loading, from 4.3 to 1.7 wt\%, lowered the number of catalytic sites and, consequently, the kinetic constants of isotope exchange by a factor from 3 to 5, while preserving the mechanism of exchange and the apparent activation energies. In contrast, the increase in the Si/Al ratio from 6 to 46 led to a change in the copper speciation to preferably monomeric sites. This resulted in a significant decrease in the exchangeability of the oxygen atoms in copper-containing mordenite and required a 200 K higher temperature for any prominent exchange rate.

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1 Introduction

Transition metal-containing zeolites belong to an important class of materials widely used as adsorbents and catalysts for various chemical transformations\(^1,2\). Among them, copper-containing zeolites have been studied in depth due to their great adsorption capacity for fuel desulphurization\(^3-5\), high catalytic activity in the decomposition of nitrogen oxides\(^6-10\) and selective catalytic reduction\(^11-15\) (SCR). The recent discovery of the selective methane oxidation to methanol over copper-containing zeolites based on the chemical looping approach\(^16-18\) brought about new opportunities for utilizing these materials for the effective valorization of natural gas.

The unique sorption and catalytic properties of the copper-containing zeolites originate from the synergetic interplay of the zeolite framework and the hosted copper-oxo species. The structural, redox and adsorption properties of the materials can be tuned over wide ranges by varying the zeolite topology\(^19-25\), Si/Al ratio\(^20,21,26-28\), copper content\(^10,29,30\), and the nature of the co-cation\(^31,32\). Depending on the conditions of the synthesis and pre-treatment, copper atoms can be stabilized in either Cu\(^{II}\) or Cu\(^{I}\) oxidation state, providing the possibility for creating the active sites for catalytic reactions\(^33-35\) or to carry out the chemical looping cycles\(^21,36,37\). Notably, the transformation between the Cu\(^{I}\) and Cu\(^{II}\) is the redox reaction, which involves the addition or removal of the oxygen atoms. They are bonded to the copper rather than the silicon or aluminum atoms and, therefore, are referred to as “extra-framework”. The total concentration of extra-framework oxygen is governed by the copper content and the nature of the copper-oxo species and, in most cases, corresponds to less than 5% of the total oxygen in the material\(^22,38-41\). At the same time, they play a key role in redox transformations, such as NOx decomposition, SCR\(^39-44\), and selective methane oxidation\(^16,36,45-49\). The highly reactive extra-framework \(\alpha\)-oxygen O\(^-\) atoms were identified as stoichiometric and catalytic sites in benzene oxidation to phenol\(^50\) and the decomposition of nitrous oxide over iron-containing ZSM-5 zeolites\(^51\). Similarly, the oxidation of methane to methanol over copper-containing zeolites occurred with the direct involvement of the extra-framework oxygen atoms, resulting in their incorporation into the reaction products as demonstrated by isotope labeling\(^45,46\). Extra-framework oxygen atoms possess higher reactivity as compared to the framework ones, including...
predisposition to isotope exchange. Moreover, the exchangeability of the oxygen atoms was frequently correlated with the catalytic activity.

In general, oxygen isotope exchange is a powerful technique for evaluating the mobility of oxygen atoms. Several methodological approaches were developed, including experiments in closed and open systems, isothermally at elevated temperature, and in temperature-programmed regime. In particular, the oxygen isotope exchange was successfully applied to investigate oxygen mobility in non-porous materials with a high oxygen storage capacity (OSC) as well as in transition metal oxides, widely used as catalysts and supports. The evaluation of the kinetics of oxygen isotope exchange enables a quantitative description of the mobility of oxygen atoms by determining the exchange mechanism, kinetic constants, corresponding activation energies and the number of exchangeable atoms. Isotope exchange also enables the estimation of diffusion coefficients for the oxygen diffusion in non-porous solids.

Among the porous materials, oxygen isotope exchange was studied over iron- and copper-containing zeolites. Panov’s group investigated isotope exchange over iron-containing ZSM-5 zeolite and showed that this material effectively catalyzes the homo-exchange between oxygen molecules in the gas phase over $\alpha$-oxygen $O^-$ radicals below 250 K. These species were previously shown to be the active sites in the decomposition of nitrogen oxides and in methane conversion to methanol. Increasing the exchange temperature to above 500 K leads to a hetero-exchange, i.e. direct involvement of the atoms from the solid in the exchange with the dioxygen molecule in the gas phase. Jia et al. studied the exchange over iron-containing ZSM-5 zeolite and concluded that mainly extra-framework atoms participate in the isotope exchange at 523 K, indicating their higher mobility with respect to framework oxygen. Interestingly, at higher temperatures the number of exchangeable oxygen atoms significantly exceeds the amount of extra-framework oxygen. Valyon et al. reported that about 13% and 33% of the oxygen atoms in copper-containing MFI and FAU, respectively, can be exchanged with the gas phase at 773 K. As reported by Leglise et al., FeMOR has around 34% of the exchangeable oxygen atoms at 773 K. Similar values were obtained in our recent study on oxygen isotope exchange over
copper-containing mordenite\textsuperscript{57}. Notably, the sodium and proton forms of zeolites do not undergo the isotope exchange under similar conditions with the prominent rate\textsuperscript{57,67}, showing that the hosted metal species induce the lability of the framework oxygen atoms. Importantly, the mechanism of the exchange depends significantly on the nature of the hosted species. Voskoboinikov et al. showed that isolated Fe\textsuperscript{3+} cations or small iron-oxo clusters in ZSM-5 zeolite induce the single-atom type of exchange, while the material with hosted larger iron-oxo clusters mainly exchanges oxygen atoms \textit{via} the two-atom exchange mechanism\textsuperscript{39}. Moreover, the kinetics of the isotope exchange over iron- and copper-containing zeolites is complicated by the presence of at least two temporary resolved processes: initial fast exchange followed by a secondary slow process\textsuperscript{39,41,42,67}. The effect of the sample composition, such as Si/Al ratio and copper content, on the isotope exchange kinetics over copper-containing zeolites has not been studied systematically thus far.

Herein, we report a study of oxygen isotope exchange over copper-containing mordenite zeolite with different copper loadings and Si/Al ratios in both temperature-programmed and isothermal regimes with subsequent kinetic modeling. A decrease in both the copper loading and the aluminum content leads to a loss of the activity in the isotope exchange, yet the effect of the Si/Al ratio is more pronounced. The exchangeability of the oxygen atoms in copper-containing mordenite is determined by the nature of the hosted copper-oxo species, which, in turn, is governed by the aluminum content in the zeolite framework\textsuperscript{24,26,28}. A previously proposed kinetic model\textsuperscript{67}, accounting for the presence “fast” and “slow” sources of exchangeable oxygen atoms, reasonably describes the kinetics of the isotope exchange over series of studied copper-containing mordenites.

2 Experimental section

2.1 Synthesis and characterization of the materials

The commercial mordenite zeolites CBV10A, CBV21A and CBV90A were purchased from Zeolyst International and were used as the starting materials. Copper-containing zeolites were prepared as follows: 5 g of commercial zeolite were mixed with 500 mL of a 0.05 M copper nitrate solution (99\%, Sigma-Aldrich) and the suspension was stirred overnight at 323 K. Afterwards, the materials were
filtered, rinsed with deionized water and dried at 393 K for 3 h. The ion-exchange procedure was repeated three times and the resulting materials were dried at 373 K for 12 h. In order to obtain an incomplete degree of ion exchange for mordenite with a Si/Al ratio of 6.5 (CBV 10A), a copper nitrate solution with a lower concentration, between 0.005 M and 0.05 M, was used, and the ion exchange procedure was performed once. The resulting copper-containing samples are referred to as “Cu(X)MOR(Y)”, where “X” corresponds to the copper content in wt% and “Y” represents the Si/Al ratio in the material.

The elemental composition in the resulting materials was determined using inductively coupled plasma mass spectrometry (ICP–MS) with an Agilent 77009 ICPMS instrument after the digestion of the samples in 1 M hydrofluoric acid.

2.2 Temperature-programed isotope exchange (TPIE) measurements

For TPIE experiments, the sample in the form of 0.25-0.5 mm fraction was placed into a tubular quartz reactor with a fixed catalyst bed and an inner diameter of 4.15 mm. The amount of used sample corresponded to 0.55 mg of copper in all the TPIE experiments. Prior to the TPIE measurements, the sample was heated in a 10 ml·min$^{-1}$ flow (at 298 K) of 5% $^{16}$O$_2$ in He (99.9999%, Messer) to 723 K at a heating rate of 10 K·min$^{-1}$, annealed for 120 min and cooled to 473 K. Thereafter the gas was switched to He/Ar/$^{16}$O$_2$/18O$_2$ (Sigma Aldrich, 99 atom % $^{18}$O) = 37/1/1/1 vol. with the total flow remaining constant. Subsequently, the sample was heated to 1100 K at a heating rate of 10 K·min$^{-1}$ and simultaneously the isotopic composition of the gas phase was measured using a Balzers QMA-200 on-line mass spectrometer (MS). Signals of m/z=32, 34, 36 were used to calculate the fractions of $^{16}$O$_2$, $^{16}$O$^{18}$O and $^{18}$O$_2$ isotopologues.

2.3 Isothermal isotope exchange (IIE)

To study the isothermal oxygen isotope exchange, a 0.25-0.5 mm fraction of the sample was placed into the quartz plug flow tubular reactor with an inner diameter of 4.15 mm. The amount of sample was 25 mg for Cu(4.3)MOR(6) and Cu(3.5)MOR(6) and 50 mg for other copper-containing mordenites. The activation of the sample was carried out by heating in 5% $^{16}$O$_2$ balanced with He (99.9999%, Messer) from ambient to the desired temperature, which was 873 K for all samples with Si/Al=6.5, 933 K for
Cu(3.4)MOR(10) and 1023 K for Cu(1.2)MOR(46). The total flow corresponded to 10 ml·min⁻¹ at 298 K for Cu(4.3)MOR(6) and Cu(3.4)MOR(10) and to 5 ml·min⁻¹ for the other samples; the heating rate was 10 K·min⁻¹ in all the experiments. The sample was annealed for additional 120 min. and subsequently cooled to the temperature of the experiment followed by additional 15 min exposure for the complete temperature stabilization. Finally, the gas flow was switched to He/Ar/¹⁸O₂ = 18/1/1 vol. mixture with the total flow remained constant. The composition of the gas phase was monitored using a Balzers QMA-200 MS, and the ion currents of m/z=32, 34, 36 and 40 were used to calculate the fractions of the ¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂ isotopologues and the input function α_{inp}, respectively.

2.4 Fitting of the isothermal oxygen isotope exchange kinetics

During the ¹⁶O/¹⁶O isotope exchange between the gas phase and the solid, the total number of all oxygen atoms remains constant, while the isotopic composition of both phases changes. To describe the isotopic composition of the solid phase, parameter α_s = \frac{N(¹⁸O_s)}{N(¹⁸O_s)+N(¹⁶O_s)} was used corresponding to the ¹⁸O atomic fraction in the solid. The gas phase composition was described using the fraction of asymmetric isotopologue ¹⁶O¹⁸O (f_{34}) and the parameter α corresponding to the fraction of ¹⁸O atoms⁶⁸,⁶⁹.

Klier⁶⁸ and Muzykantov⁶⁹ were the first to propose the theory of the oxygen isotope exchange kinetics between the gas phase and the solid. Depending on the number of oxygen atoms from the solid participating in the exchange reaction, zero-atom (R⁰), single-atom (R¹) and two-atom (R²) kinetically distinct types of exchange were suggested. We previously showed that the isothermal oxygen isotope exchange over copper-containing mordenite can be adequately described using the kinetic model with two independent sources of exchangeable oxygen, which undergo both R¹ and R² types of exchange⁶⁷.

The corresponding set of partial differential equations (PDE) is the following:

\[
\frac{\partial \alpha(t,l)}{\partial t} = -\frac{1}{\tau} \frac{\partial \alpha(t,l)}{\partial l} - \frac{1}{2} \cdot C(O)_{fast} \cdot (k_{fast}^1 + C(O)_{fast} \cdot k_{fast}^2) (\alpha - a_{fast}) - \frac{1}{2} \cdot C(O)_{slow} \cdot (k_{slow}^1 + C(O)_{slow} \cdot k_{slow}^2) (\alpha - a_{slow})
\]

\[
\frac{\partial f_{34}(t,l)}{\partial t} = -\frac{1}{\tau} \frac{\partial f_{34}(t,l)}{\partial l} - C(O)_{fast} [k_{fast}^1 (\alpha (1 - a_{fast}) + a_{fast} (1 - \alpha) - f_{34}) + C(O)_{fast} k_{fast}^2 (2a_{fast} (1 - a_{fast}) - f_{34})] -
\]
\[-C(O)_\text{slow}[k^1_{\text{slow}}(\alpha(1-a_{\text{slow}})+a_{\text{slow}}(1-\alpha)-f_{34})+C(O)_{\text{slow}}k^2_{\text{slow}}(2a_{\text{slow}}(1-a_{\text{slow}})-f_{34})]\]

\[
\frac{\partial \alpha_{\text{fast}}(t,l)}{\partial t} = C(O)_2 \text{gas} \left( k^1_{\text{fast}} + C(O)_{\text{fast}} \cdot k^2_{\text{fast}} \right) (\alpha - \alpha_{\text{fast}})
\]

\[
\frac{\partial \alpha_{\text{slow}}(t,l)}{\partial t} = C(O)_2 \text{gas} \left( k^1_{\text{slow}} + C(O)_{\text{slow}} \cdot k^2_{\text{slow}} \right) (\alpha - \alpha_{\text{slow}})
\]

with the following initial and boundary conditions:

\[t = 0: \quad \alpha = f_{34} = \alpha_{\text{fast}} = \alpha_{\text{slow}} = 0\]

\[l = 0: \quad \alpha = \alpha_{\text{input}}; \quad f_{34} = f_{34} \text{input}\]

Here \(C(O)_2 \text{gas}\) represents the concentration of the oxygen molecules in the gas phase, \(\alpha_{\text{fast}}\) and \(\alpha_{\text{slow}}\) are the fraction of \(^{18}\text{O}\) atoms in the “fast” and “slow” source, respectively; and \(C(O)\) (mol·l\(^{-1}\)), \(k^1\) (l·mol\(^{-1}\)·s\(^{-1}\)) and \(k^2\) (l\(^2\)·mol\(^{-2}\)·s\(^{-1}\)) are the concentration of exchangeable oxygen atoms and kinetic constants of single-atom and two-atom exchange, respectively. The lower indices correspond to the “fast” and the “slow” oxygen sources, respectively.

Quantification of the kinetic parameters was performed by means of fitting of the experimental data according to the model described above. The fitting was carried out using Wolfram Mathematica 12 software\(^{70}\) by minimizing the normalized root-mean square deviation (NRMSD):

\[
\text{NRMSD} = \sqrt{\frac{1}{t_{\text{max}}-t_0} \int_{t_0}^{t_{\text{max}}} \left( \frac{\alpha_{\text{calc}}-\alpha_{\text{exp}}}{\alpha_{\text{exp}}} \right)^2 + \left( \frac{f_{34,\text{calc}}-f_{34,\text{exp}}}{f_{34,\text{exp}}} \right)^2 dt}
\]

3 Results

Table 1 presents the chemical composition of all the samples. The copper weight loading in Cu(x)MOR(6) samples ranged from 1.7 to 4.3 wt\%, corresponding to the Cu/Al ratio from 0.14 to 0.38. The copper loading in the zeolite with the Si/Al ratio of 10 was 3.4 wt\% and in the sample with ratio of 46 it was 1.2 wt\%. The resulting Cu/Al ratio is 0.38, 0.39 and 0.6 for Cu(4.3)MOR(6), Cu(3.5) MOR(10) and Cu(1.2) MOR(46), respectively. These values are close to the theoretical limit of 0.5, indicating a high degree of ion exchange and a presence of copper species as counter ions for ion exchange positions in the corresponding samples.
Figure 1 shows the fraction of the $^{16}$O$^{18}$O isotopologue during TPIE experiments. Below 700 K, the isotopic composition of the gas phase remains constant for all samples, therefore, the rate of isotope exchange is negligible. At higher temperature, single-labeled oxygen molecules appear in the gas phase, indicative of the occurrence of isotope exchange. However, different samples yield a different temperature for the initiation of the isotope exchange. Over all the Cu(x)MOR(6) samples with Si/Al = 6.5 single-labeled oxygen was detected starting at 750 K (Figure 1 A), while over Cu(3.4)MOR(10) and Cu(1.2)MOR(46) temperatures of 850 K and 950 K were required (Figure 1 B). While the initiation of the exchange process over all the Cu(x)MOR(6) samples occurs at a similar temperature, a decrease in the copper content in the material slows down the exchange rate. At about 1100 K all the Cu(x)MOR(6) samples almost completely convert the initial isotopic composition of the gas phase to the equilibrium mixture. Cu(3.4)MOR(10) and Cu(1.2)MOR(46) showed different a behavior: a higher temperature is necessary to achieve the equilibrium isotope distribution in the gas phase.

Figure 2 presents the experimental curves for $f_{34}$ (dashed lines) and $\alpha$ (solid lines) for the IIE experiments. The different temperature ranges were selected for determining the isothermal kinetics of exchange based on the results of TPIE experiments so that the exchange rate in all the experiments was sufficient to be detected and Arrhenius analyses could be performed: i) 793 - 893 K for Cu(x)MOR(6) samples with different copper content; ii) 873 - 933 K for Cu(3.4)MOR(10), and iii) 973 - 1048 K for Cu(1.7)MOR(46). After the switch from unlabeled to isotopically labeled oxygen, the parameter $\alpha$ rapidly increased to the certain value, which depends on the temperature and the composition of the sample, and then slowly tended to unity. During the whole experiment, the $\alpha$ value was lower than one indicating the ongoing exchange process between the initially fully labeled gas phase and the unlabeled solid sample. In turn, parameter $f_{34}$ increased rapidly after the switch, reached a maximum and then slowly tended to zero value. Despite the general similarity of the behavior of both $\alpha$ and $f_{34}$, the exchange temperature and the sample composition significantly affected the shape of the curves for both parameters, probably due to differences in the kinetic constants and the concentration of the exchangeable oxygen atoms in the materials. To quantitatively estimate the effect of the exchange temperature, the copper
content, and the Si/Al ratio on the intrinsic kinetic parameters, we fitted the experimental data using the model with “fast” and “slow” sources of the exchangeable oxygen (Figures S1-S6). The quality of the fits was high (NRMSD parameter varied from 0.01 to 0.06), resulting in close matches between the experimental and corresponding fitted curves, hence enabling the application of this model to describe the kinetics of the isotope exchange. The residual misfit may be associated with some physical phenomena, which were not accounted for, such as temperature gradients in the reactor, the effect of longitudinal gas diffusion, and non-laminar gas flow. Table 2 lists the fitted kinetic parameters together with the errors and the resulting NRSMD functional values.

Figure 3 presents the concentrations (A, D) and the kinetic constants (B, C, E and F) corresponding to “fast” and “slow” sources of exchangeable atoms for the Cu(x)MOR(6) samples. The amount of exchangeable oxygen in the “fast” and “slow” sources for all the Cu(x)MOR(6) samples comprises 1.8±0.3 and 5.2±0.4 mol·l⁻¹, respectively. Given that the total concentration of the oxygen atoms in the samples is between 19 and 20 mol·l⁻¹ (for a bulk density of 0.6 kg·l⁻¹), these values correspond to 9±1.5% and 25±2% of the total oxygen content in the material, clearly showing the involvement of the framework oxygen atoms in the isotope exchange. Interestingly, the amount of exchangeable oxygen corresponding to both the “fast” and the “slow” sources is independent of the reaction temperature or the copper content. At the same time, “fast” and “slow” sources demonstrate very different kinetic behavior. Thus, the $R^2$ type of exchange prevails for the “fast” source and $R^l$ dominates for the “slow” source (Table 2). For instance, over Cu(4.3)MOR(6) at 873 K the initial rates of the single-atom and two-atom types of isotope exchange for the “fast” source are 1.2 and 4.4 mmol·l⁻¹·s⁻¹, respectively, while the corresponding values for the “slow” source are 2.0 and 1.0 mmol·l⁻¹·s⁻¹. The estimation of the constants corresponding to the marginal type of isotope exchange cannot be carried out with sufficient accuracy for the further analysis of the apparent activation energy. Therefore, the Arrhenius analysis was performed for the prevailing mechanism of exchange, namely two-atom for the “fast” source and single-atom for the “slow” source (Figures 4 A and B). The decrease in the copper loading in the Cu(x)MOR(6) samples has no effect on the apparent activation energy, which correspond
to 93±26 kJ·mol⁻¹ and 115±16 kJ·mol⁻¹ for the two-atom exchange of the “fast” source and single-atom of the “slow” source, respectively. At the same time, the decrease in the copper content leads to the decrease in the absolute value of the kinetic constants for both sources (Table 2). Thus, the $k_{fast}^2$ decreased from 1.62 l²·mol⁻²·s⁻¹ for Cu(4.3)MOR(6) to 0.44 l²·mol⁻²·s⁻¹ for Cu(1.7)MOR(6). Similarly, $k_{slow}^1$ decreased from 0.56 l·mol⁻¹·s⁻¹ to 0.13 l·mol⁻¹·s⁻¹.

As mentioned above, a direct comparison of the kinetic constants corresponding to the samples with different Si/Al ratios is ambiguous since the experiments were performed at significantly different temperatures. Nonetheless, the temperature and the copper loading have no prominent effect on the concentration of the exchangeable oxygen atoms in these samples. Figure 5 demonstrates the concentration of oxygen atoms corresponding to the “slow” and “fast” sources for the samples with different Si/Al ratios. A lower aluminum content leads to a decrease in the number of oxygen atoms due to the “fast” source, while the concentration of “slow” source persists. Figure 6 A) and B) illustrates the Arrhenius plots for two-atom exchange type of the “fast” source and single-atom exchange of the “slow” source over Cu(4.3)MOR(6), Cu(3.4)MOR(10) and Cu(1.2)MOR(46). In contrast to the variation in the copper loading, the variation in the aluminum content brought about a significant change in the apparent activation energy: $E_a = 93±26$ kJ·mol⁻¹, 53±25 kJ·mol⁻¹ and 37±13 kJ·mol⁻¹ for the two-atom exchange of the “fast” source over Cu(4.3)MOR(6), Cu(3.4)MOR(10) and Cu(1.2)MOR(46), respectively. The corresponding apparent activation energy for the single-atom exchange of the “slow” source were 115±16 kJ·mol⁻¹, 170±35 kJ·mol⁻¹ and 62±18 kJ·mol⁻¹.

4 Discussion

The TPIE experiments show that both copper content and Si/Al ratio affect the exchangeability of the oxygen atoms in copper-containing mordenite (Figure 1). However, the variation in the aluminum content has the stronger effect than the copper loading. Thus, in the case of the CuMOR samples with Si/Al = 6.5, a decrease in the copper content from 4.3 to 1.4 wt% leads to a shift in the exchange curve of about 50 K towards higher temperature, while a shift of about 200 K was observed from
Cu(4.3)MOR(6) to Cu(1.2)MOR(46). Similar trends were observed previously for the autoreduction of copper in inert atmosphere over the same set of copper-containing mordenites\textsuperscript{22}. This noticeable effect of the aluminum content was associated with the change of copper speciation\textsuperscript{22,26}: mordenite with a high Si/Al preferably stabilizes monomeric copper species, while a higher aluminum content tends to favor the formation of dimeric and lager copper-oxo clusters\textsuperscript{24,26,28}. At the same time, in the copper-containing mordenite with fixed a Si/Al ratio, copper loading did not have a prominent effect on copper speciation, as revealed by FTIR of adsorbed nitrogen monoxide and EXAFS spectroscopy\textsuperscript{22,24}. Thus, the kinetics of the isotope exchange of the framework oxygen atoms is governed by the structure of the copper-oxo species in the zeolite pores. We suggest that copper dimers could more efficiently induce the lability of the framework oxygen as compared to monomeric species. As a result, lower temperature is required to initiate isotope exchange over CuMOR with a high aluminum content. The reducibility of the different copper species coincides with their tendency to induce isotope exchange of the framework oxygen atoms\textsuperscript{22,26}. This makes temperature-programmed oxygen exchange a promising tool for indirect characterization of the redox properties of copper species.

The decrease in the copper loading of the materials with a fixed aluminum content leads to a decrease of the kinetic constants of exchange, while the number of the exchangeable oxygen atoms and the apparent activation energy of the exchange are not affected (Table 2, Figure 3). This contradicts the previously proposed model, which suggests the induction of the exchange of some part of the framework oxygen atoms in the close proximity to metal-oxo species, and formation of a “pool” of exchangeable oxygen atoms\textsuperscript{39,44}. Consequently, the total number of exchangeable oxygen atoms should be proportional to the copper loading, which is not the case with our samples. Instead, the increase in the copper content exclusively leads to the increase in all the kinetic constants. Therefore, we conclude that the number of exchangeable atoms in the framework is determined by the zeolite structure, and the hosted copper-oxo species act as catalytic sites in the exchange reaction. As a result, the increase in the copper loading increases the number of active sites resulting in an increase in the rate of reaction. Simultaneously, for all the Cu(x)MOR(6) samples the $R^2$ and $R^1$ types of exchange prevail for the “fast” and “slow” sources,
respectively. Moreover, the apparent activation energies are neither affected by the variation of the copper loading. In summary, we suggest that the mechanisms of the exchange reaction are similar over the mordenite samples with different copper contend and a fixed Si/Al ratio. \textit{A priori}, the mechanism of the catalytic reaction is determined by the structure of the catalyst, i.e. copper-oxo species for the isotope exchange reaction. Similarity of the mechanism indicates the similarity of the nature of the copper-oxo species in the corresponding samples. This is in good agreements with previous reports on the structure of the copper sites\textsuperscript{22,24}.

In contrast to the variation in the copper loading, the decrease in the aluminum content significantly reduces the overall activity of the materials in the oxygen isotope exchange, meaning that a higher temperature is required to achieve comparable values for the kinetic constants of exchange, in agreement with TPIE experiments. Apart from that, the $R^2$ type of exchange begins to prevail for the “slow” source. Moreover, the apparent activation energies differ significantly for the samples with various aluminum content (Figure 6). Thus, values of $E_a$ of 96±26, 37±13 and 53±25 kJ·mol\textsuperscript{-1} were found for the two-atom exchange type of the “fast” source over Cu(4.3)MOR(6), Cu(3.4)MOR(10) and Cu(1.2)MOR(46), respectively. The corresponding values for the single-atom exchange of the “slow” source are 115±16, 62±18 and 170±35 kJ·mol\textsuperscript{-1}, respectively. A significantly different apparent activation energy indicates a different mechanism of the isotope exchange reaction, which we associate with the presence of active sites, i.e. the copper-oxo species of different structure. Indeed, in the copper-containing mordenite with a low Si/Al ratio of 6.5 copper dimers were found, while material with a Si/Al ratio of 46 contains a large fraction of monomeric copper species\textsuperscript{24,26,28}. Different copper sites have a different catalytic activity in the isotope exchange reaction resulting in changes in the reaction mechanisms and apparent activation energy. The variation in the aluminum content also affects the concentration of the oxygen atoms in the “fast” source. Specifically, in the sample with the lowest aluminum content, the concentration of the “fast” source decreases to 3\% of the total oxygen. Simultaneously, the concentration of the “slow” source is similar in all the studied samples and is independent of the copper or aluminum content of the material. The sum of the “slow” and “fast” sources
results in the total amount of exchangeable oxygen atoms around 35±5% of the total oxygen content in the zeolite for all the samples, which is close to the 34% previously reported by Leglise for iron-containing mordenite\textsuperscript{42}. This indicates that only some of the oxygen atoms in the zeolite framework have the intrinsic possibility of participating in the isotope exchange. The reasons for the unequal exchangeability of the oxygen atoms might be associated with the different location in the zeolite structure.

In the MOR structure, linked four- and five-membered rings (MR) form 12 MR main channels interconnected by 8 MR side pockets\textsuperscript{71} (Figure S7) resulting in four non-equivalent T-positions and 10 inequivalent oxygen positions\textsuperscript{71}. \textit{A priori}, oxygen atoms located in the different sites may have different activity in the isotope exchange. Moreover, aluminum atoms preferentially occupy T3 and T4 positions, located at the intersection of 12 MR and side pockets; hence, they can affect the structure and location of copper species and other charge-balancing cations in the pore system\textsuperscript{32,72}. We were unable to derive the linear correlation of the kinetically “fast” and “slow” oxygen sources with the structural composition of the copper-exchange zeolite. We speculate that “fast” may be associated with oxygen atoms, connected to aluminum, while “slow” source may include the oxygen atoms that have only silicon neighbors. This is in agreement with the lower temperature required for oxygen isotope exchange over gamma-alumina or proton form of ZSM-5 zeolite as compared to pure silicame\textsuperscript{57,61,73}. However, the establishment of the exact nature of the exchangeable atoms in the zeolite framework is currently impossible.

5 Conclusions

In conclusion, we showed the effect of the copper loading and Si/Al ratio on the oxygen isotope exchange over copper-containing mordenite. According to temperature-programmed isotope exchange, the decrease in the copper loading in the samples with a similar Si/Al ratio only slightly decreases the activity in the oxygen isotope reaction, while the decrease in the aluminum content lowers the activity significantly. The quantitative analysis of the isothermal exchange kinetics shows that the variation of the copper loading affects the absolute value of the kinetic constants and does not influence the apparent activation energies of the isotope exchange reaction. In contrast, the oxygen isotope exchange proceeds
via a different mechanism over the samples with a different Si/Al ratio. The total fraction of the exchangeable atoms comprises around 35% of the total amount of oxygen content and does not depend on the exchange temperature. The exchangeable atoms may be divided into “fast” and “slow” sources, and the concentration of the former is proportional to the aluminum content, while the concentration of latter is independent on the composition of material.

The isotope exchange of the framework oxygen atoms in copper-containing mordenite is catalyzed by hosted copper-oxo species, and the dimeric copper sites are more efficient catalytic sites as compared to copper monomers. Notably, the overall activity of the materials in the isotope exchange correlates with the reducibility of the hosted copper-oxo species. This makes oxygen isotope exchange a powerful tool for studying the copper-exchanged zeolites and, possibly, other metal-containing molecular sieves.

6 Supporting information

Experimental data points and fitted curves for isotope exchange experiments over copper-containing mordenites with various copper loadings and Si/Al ratios, different crystallographic positions for T sites and O atoms in MOR framework.

7 Acknowledgements

V.L.S. and J.A.v.B thank the Energy System Integration platform of the Paul Scherrer Institute for financial support. J.A.v.B. and M.A.A. thank the SNF for financial support (project 200021_178943).

8 References


https://doi.org/10.1021/JACS.7B06472.


Solid O


(70) Mathematica, version 12.0; software for technical computation; Wolfram Research: Champaign, IL, 2020.


Table 1. Chemical composition of the studied copper-containing mordenite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu content, wt %</th>
<th>Na content, wt %</th>
<th>Si/Al atomic ratio</th>
<th>Cu/Al atomic ratio</th>
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</thead>
<tbody>
<tr>
<td>Cu(4.3)MOR(6)</td>
<td>4.36</td>
<td>1.22</td>
<td>6.5</td>
<td>0.38</td>
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<tr>
<td>Cu(3.5)MOR(6)</td>
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<td>6.5</td>
<td>0.31</td>
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<td>Cu(2.5)MOR(6)</td>
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<td>2.73</td>
<td>6.5</td>
<td>0.21</td>
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<td>Cu(3.4)MOR(10)</td>
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<td>&lt;0.01</td>
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Table 2. Kinetic parameters and the resulting NRMSD value, obtained by fitting of the isothermal isotope exchange experiments over copper-containing mordenite samples. Concentration of the sources has dimension mol·L⁻¹·s⁻¹, kinetic constants $k_1$ and $k_2$ - 1·mol⁻¹·s⁻¹ and 1²·mol⁻²·s⁻¹, respectively.

<table>
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<tr>
<th>Sample</th>
<th>T, K</th>
<th>$C(O)_{fast}$</th>
<th>$k_{fast}^1$</th>
<th>$k_{fast}^2$</th>
<th>$C(O)_{slow}$</th>
<th>$k_{slow}^1$</th>
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<td>0.43±0.09</td>
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<td>0.11±0.01</td>
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<tr>
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<td>813</td>
<td>1.8±0.17</td>
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<td>0.65±0.13</td>
<td>5.0±0.24</td>
<td>0.18±0.02</td>
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<td>5.0±0.24</td>
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<td>853</td>
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**Figure captures**

Fig. 1. The fraction of the single-labeled $^{16}$O$^{18}$O isotopologue during TPIE experiments over A) the Cu(x)MOR(6) samples with different copper loading and B) copper-containing mordenite samples with various Si/Al ratios.

Fig. 2. Experimental curves for $\alpha$ (solid lines) and $f_{34}$ (dashed lines) during isothermal isotope exchange experiments performed at different temperatures over the copper-containing mordenite samples.

Fig. 3. Kinetic parameters of the oxygen isotope exchange in the Cu(x)MOR(6) samples with different copper loadings. Subfigures A)-C) correspond to concentration of exchangeable oxygen and kinetic constant for the “fast” source, and subfigures D)-F) represent data for the “slow” source.

Fig. 4. Arrhenius plots for A) two-atom exchange type of the “fast” source and B) single-atom exchange of the “slow” source over Cu(x)MOR(6) samples with different copper loading.

Fig. 5. The fractions of exchangeable oxygen corresponding to the “fast” and “slow” sources for copper-containing mordenite samples with different Si/Al ratio.

Fig. 6. Arrhenius plots for A) two-atom exchange of the “fast” source and B) single-atom exchange of the “slow” source over copper-containing mordenites with a different aluminum content.
Fig. 1.
Fig. 2
Fig. 3
Fig. 4

A) $E_a = 93 \pm 26 \text{ kJ mol}^{-1}$

B) $E_a = 115 \pm 16 \text{ kJ mol}^{-1}$
Fig. 5
Fig. 6

A) $E_a = 53 \pm 25 \text{ kJ/mol}$

B) $E_a = 115 \pm 16 \text{ kJ/mol}$

$E_a = 37 \pm 13 \text{ kJ/mol}$

$E_a = 62 \pm 18 \text{ kJ/mol}$

$E_a = 170 \pm 35 \text{ kJ/mol}$