Supporting Information

Title

Site-specific Xe Additions into Cu–ZSM-5 Zeolite

Authors

Takashi Yumura,[†,*] Hiroki, Yamashita,[†] Hiroe, Torigoe,[‡]
Hisayoshi Kobayashi,[†] and Yasushige Kuroda[‡]

Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan, and
Department of Fundamental Material Science, Division of Molecular and Material Science, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Kita-ku,Okayama 700-8530, Japan

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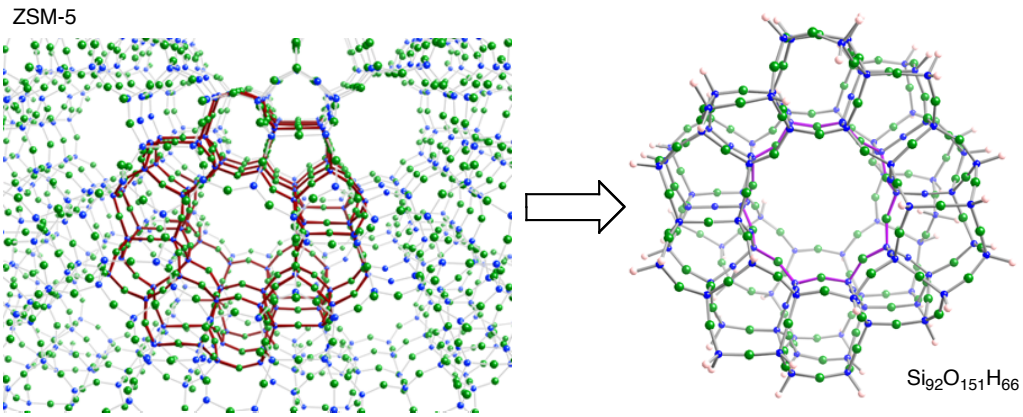

Figure S1. ZSM-5 modeling.

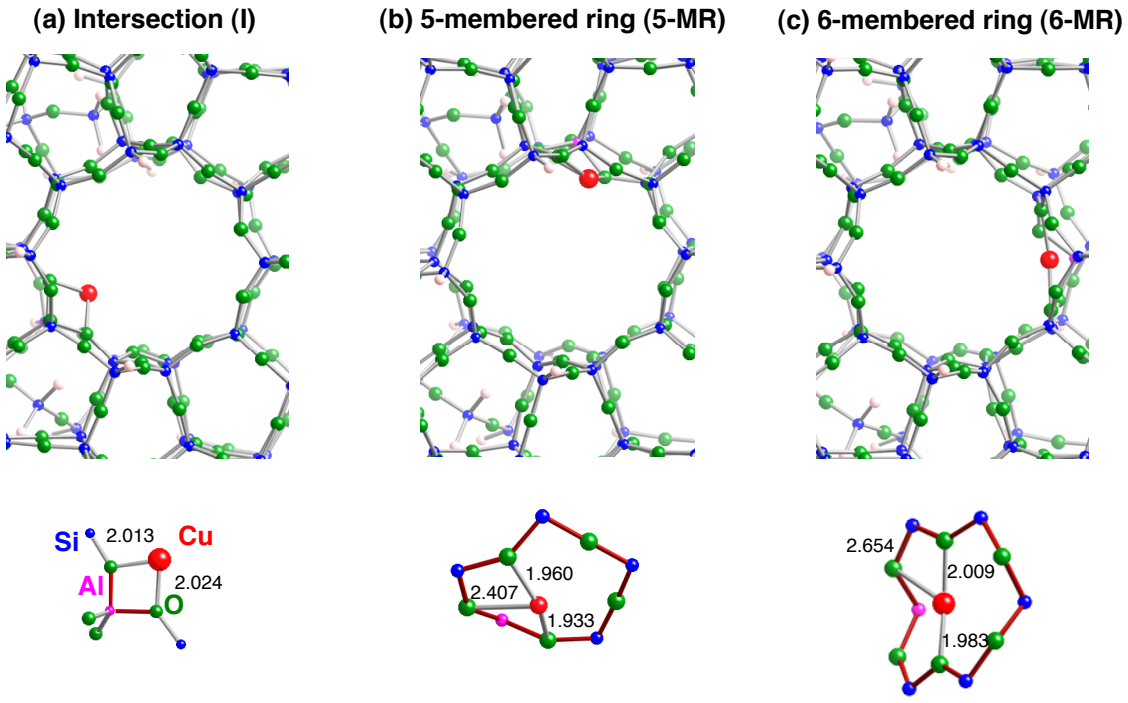

Figure S2. Three optimized geometries of a copper cation siiting inside ZSM-5. (a) the copper cation sits at the intersection between a straight and a zigzag channels. (b) the copper cation sits above a 5-membered ring of a wall along a straight channel. (c) the copper cation sits above a 6-membered ring of the wall. Their coordination environments are also seen Bond lengths are in Å.

Table S1 Electronic configurations of the small Na-ZSM-5 model based on natural atomic orbital analyses (NPA).

	Method	Electronic configuration	
Na^+ (before bonding)	B3LYP	3*s* (0.03)	3*p* (0.03)
Xe (before bonding)		5*s* (2.00)	5*p* (6.00)
Na^+ (after bonding)		3*s* (0.05)	3*p* (0.07)
Xe (after bonding)		5*s* (1.98)	5*p* (5.97)
ΔNa^a		3*s* (0.02)	3*p* (0.04)
ΔXe^b		5*s* (–0.02)	5*p* (–0.03)
Na^+ (before bonding)	MP2	3*s* (0.02)	3*p* (0.02)
Xe (before bonding)		5*s* (2.00)	5*p* (6.00)
Na^+ (after bonding)		3*s* (0.03)	3*p* (0.05)
Xe (after bonding)		5*s* (1.98)	5*p* (5.98)
ΔNa^a		3*s* (0.01)	3*p* (0.03)
ΔXe^b		5*s* (–0.02)	5*p* (–0.02)

[a] ΔNa: differences in the electron density of the extraframework Na^+ cation between before and after the Xe binding. A positive ΔNa value indicates a increase in the electron density by the Xe binding.

[b] ΔXe: differences in the electron density of the Xe atom between before and after the Xe binding. A positive ΔXe value indicates a increase in the electron density by the Xe binding.

Table S2 Electronic configurations of the small Li-ZSM-5 model based on natural atomic orbital analyses (NPA).

	Method	Electronic configuration
Li^+ (before bonding)	B3LYP	2*s* (0.03) 2*p* (0.08)
Xe (before bonding)		5*s* (2.00) 5*p* (6.00)
Li^+ (after bonding)		2*s* (0.07) 2*p* (0.17)
Xe (after bonding)		5*s* (1.97) 5*p* (5.94)
ΔLi^a		2*s* (0.04) 2*p* (0.09)
ΔXe^b		5*s* (–0.03) 5*p* (–0.06)
Li^+ (before bonding)	MP2	2*p* (0.06) 3*s* (0.03)
Xe (before bonding)		5s (2.00) 5*p* (6.00)
Li^+ (after bonding)		2s (0.06) 2*p* (0.07) 3*p* (0.07)
Xe (after bonding)		5s (1.97) 5*p* (5.95)
ΔLi^a		2s (0.06) 2*p* (0.01) 3s (–0.03) 3*p* (0.07)
ΔXe^b		5*s* (–0.03) 5*p* (–0.05)

[a] ΔLi: differences in the electron density of the extraframework Li^+ cation between before and after the Xe binding. A positive ΔLi value indicates a increase in the electron density by the Xe binding.

[b] ΔXe: differences in the electron density of the Xe atom between before and after the Xe binding. A positive ΔXe value indicates a increase in the electron density by the Xe binding.

Table S3 Electronic configurations of the Na-ZSM-5 model in Fig. 4 based on natural atomic orbital analyses (NPA).

	Cation sites[a]	Electronic configuration
Na^+ (before bonding)	I	3*s* (0.02) 3*p* (0.08) 4*s* (0.01) 4*p* (0.02)
Xe (before bonding)		5s (2.00) 5*p* (6.00)
Na^+ (after bonding)		3*s* (0.07) 3*p* (0.14) 4*p* (0.02)
Xe (after bonding)		5*s* (1.97) 5*p* (5.96) 5*d* (0.02) 6*p* (0.01)
ΔNa[b]		3*s* (0.05) 3*p* (0.06) 4*s* (–0.01)
ΔXe[c]		5*s* (–0.03) 5*p* (–0.04) 5*d* (0.02) 6*p* (0.01)
Na^+ (before bonding)	5-MR	3*s* (0.07) 3*p* (0.13) 4*p* (0.03)
Xe (before bonding)		5s (2.00) 5*p* (6.00)
Na^+ (after bonding)		3*s* (0.10) 3*p* (0.23) 4*s* (0.01) 4*p* (0.02)
Xe (after bonding)		5*s* (1.96) 5*p* (5.94) 5*d* (0.02) 6*p* (0.01)
ΔNa[b]		4*s* (0.03) 3*d* (0.10) 4*s* (0.01) 4*p* (–0.01)
ΔXe[c]		5*s* (–0.04) 5*p* (–0.06) 5*d* (0.02) 6*p* (0.01)
Na^+ (before bonding)	6-MR	3*s* (0.10) 3p (0.24) 4*p*(0.02)
Xe (before bonding)		5s (2.00) 5*p* (6.00)
Na^+ (after bonding)		3*s* (0.13) 3*p*(0.34) 4*s*(0.01) 4*p*(0.02)
Xe (after bonding)		5*s*(1.95) 5*p*(5.94) 5*d* (0.01) 6*p* (0.01)
ΔNa[b]		3*s* (0.03) 3*p*(0.10) 4*s*(0.01)
ΔXe[c]		5*s* (–0.05) 5*p* (–0.06) 5*d* (0.01) 6*p* (0.01)

[a]Cation sites: the I, 5-MR, and 6-MR configurations are defined in Fig. 1.

[b]ΔNa: differences in the electron density of the extraframework Na^+ cation between before and after the Xe binding. A positive ΔNa value indicates a increase in the electron density by the Xe binding.

[c]ΔXe: differences in the electron density of the Xe atom between before and after the Xe binding. A positive ΔXe value indicates a increase in the electron density by the Xe binding.

Table S4 Electronic configurations of the Li-ZSM-5 model in Fig. 3 based on natural atomic orbital analyses (NPA).

	Cation sites[a]	Electronic configuration
Li^+ (before bonding)	I	2*s* (0.04) 2*p* (0.09) 3*p* (0.02)
Xe (before bonding)		5s (2.00) 5*p* (6.00)
Li^+ (after bonding)		2*s* (0.08) 2*p* (0.17) 3*s* (0.01) 3*p* (0.01)
Xe (after bonding)		5s (1.97) 5*p* (5.94) 5*d* (0.02) 6*p* (0.01)
ΔLi[b]		2*s* (0.04) 2*p* (0.08) 3*s* (0.01) 3*p* (–0.01)
ΔXe[c]		5*s* (–0.03) 5*p* (–0.06) 5*d* (0.02) 6*p* (0.01)
Li^+ (before bonding)	5-MR	2*s* (0.16) 2*p* (0.36) 3*s* (0.01) 3*p* (0.02)
Xe (before bonding)		5s (2.00) 5*p* (6.00)
Li^+ (after bonding)		2s (0.16) 2p (0.35) 3*s* (0.01) 3p (0.02)
Xe (after bonding)		5s (1.99) 5*p* (5.99) 5*d* (0.01) 6*p* (0.01)
ΔLi[b]		2*p* (–0.01)
ΔXe[c]		5s (–0.01) 5*p* (–0.01) 5*d* (0.01) 6*p* (0.01)
Li^+ (before bonding)	6-MR	2*s* (0.15) 2*p* (0.35) 3*s* (0.01) 3*p* (0.02) 4*s* (0.01)
Xe (before bonding)		5s (2.00) 5*p* (6.00)
Li^+ (after bonding)		2s (0.15) 2p (0.38) 3s (0.01) 3*p* (0.02)
Xe (after bonding)		5s (1.98) 5p (5.96) 5*d* (0.01) 6*p* (0.01)
ΔLi[b]		2p (0.03) 4*s* (0.01)
ΔXe[c]		5*s* (–0.02) 5*p* (–0.04) 5*d* (0.01) 6*p* (0.01)

[a]Cation sites: the I, 5-MR, and 6-MR configurations are defined in Fig. 1.

[b]ΔLi: differences in the electron density of the extraframework Li^+ cation between before and after the Xe binding. A positive ΔLi value indicates a increase in the electron density by the Xe binding.

[c]ΔXe: differences in the electron density of the Xe atom between before and after the Xe binding. A positive ΔXe value indicates a increase in the electron density by the Xe binding.

Full authors list in Ref. 54.

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