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The influence of silicon on the catalytic properties of CuSAPO-5 towards the selective reduction of NO_x in the presence of propene.

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Since the establishment of CuZSM-5 materials high activity for the decomposition of NO_x in the presence of hydrocarbons (SCR-HC) there has been a great interest in copper materials and their catalytic properties.¹ The mechanism for selective nitric oxide reduction on conventionally ion-exchanged zeolites is believed to occur via the reduced Cu^I form.²⁻⁴ Presence of Cu^I is easily detectable using XAS due to a strong pre-edge feature in addition to information obtained about the local structures about the target atoms.

We have collected XAS data on CuSAPO-5 prepared with varying copper and silicon contents. Samples were pre-treated sequentially with oxidising or reducing agents in an in-situ cell previous to data collection to establish the presence of a Cu²⁺/Cu⁺ red-ox pair. The XANES data gives direct information about the oxidation state of copper in the materials (Fig 1 and 2).

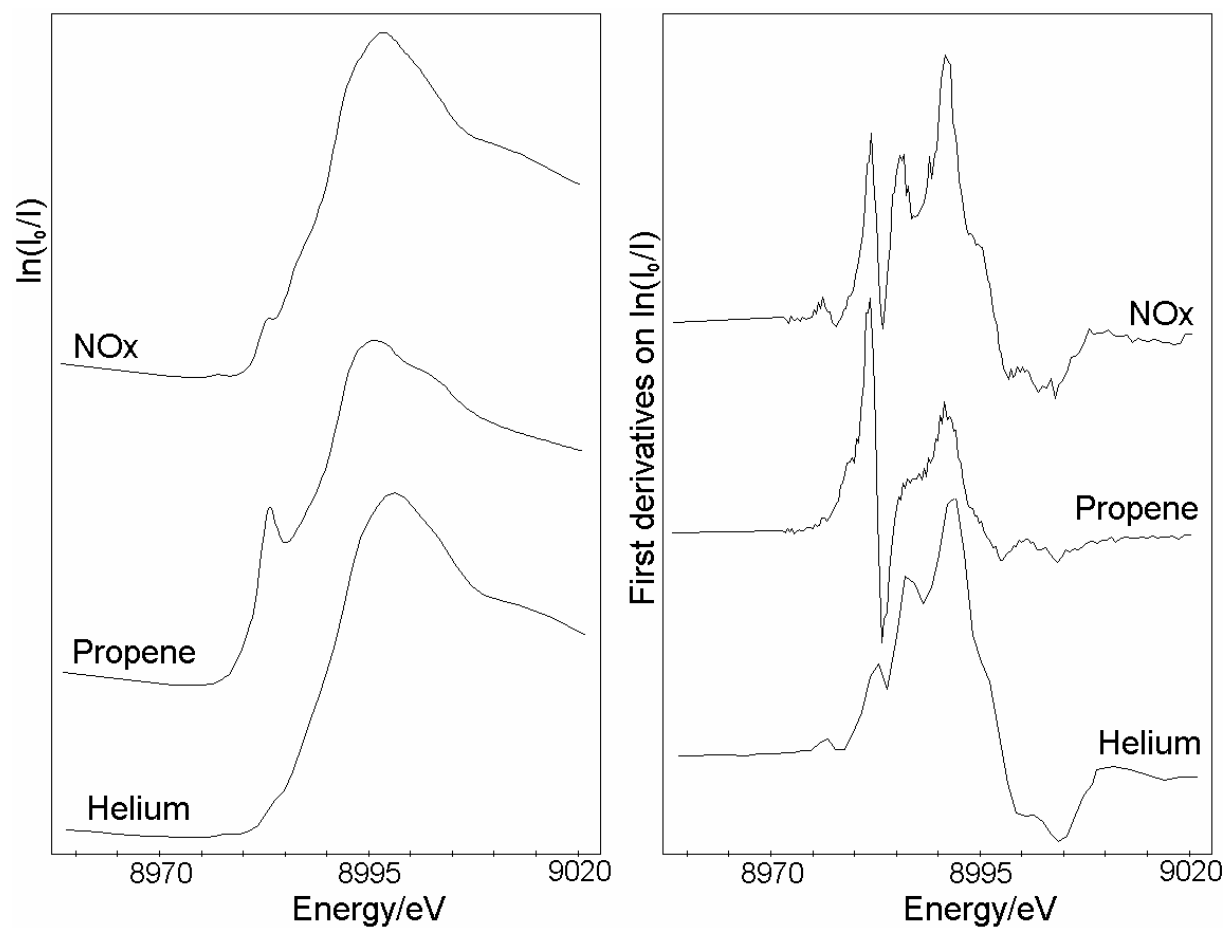


Figure 1 Normalised Cu K-edge XANES of the low copper content CuSAPO-5 system heated in helium, treated in propene and finally NOx.

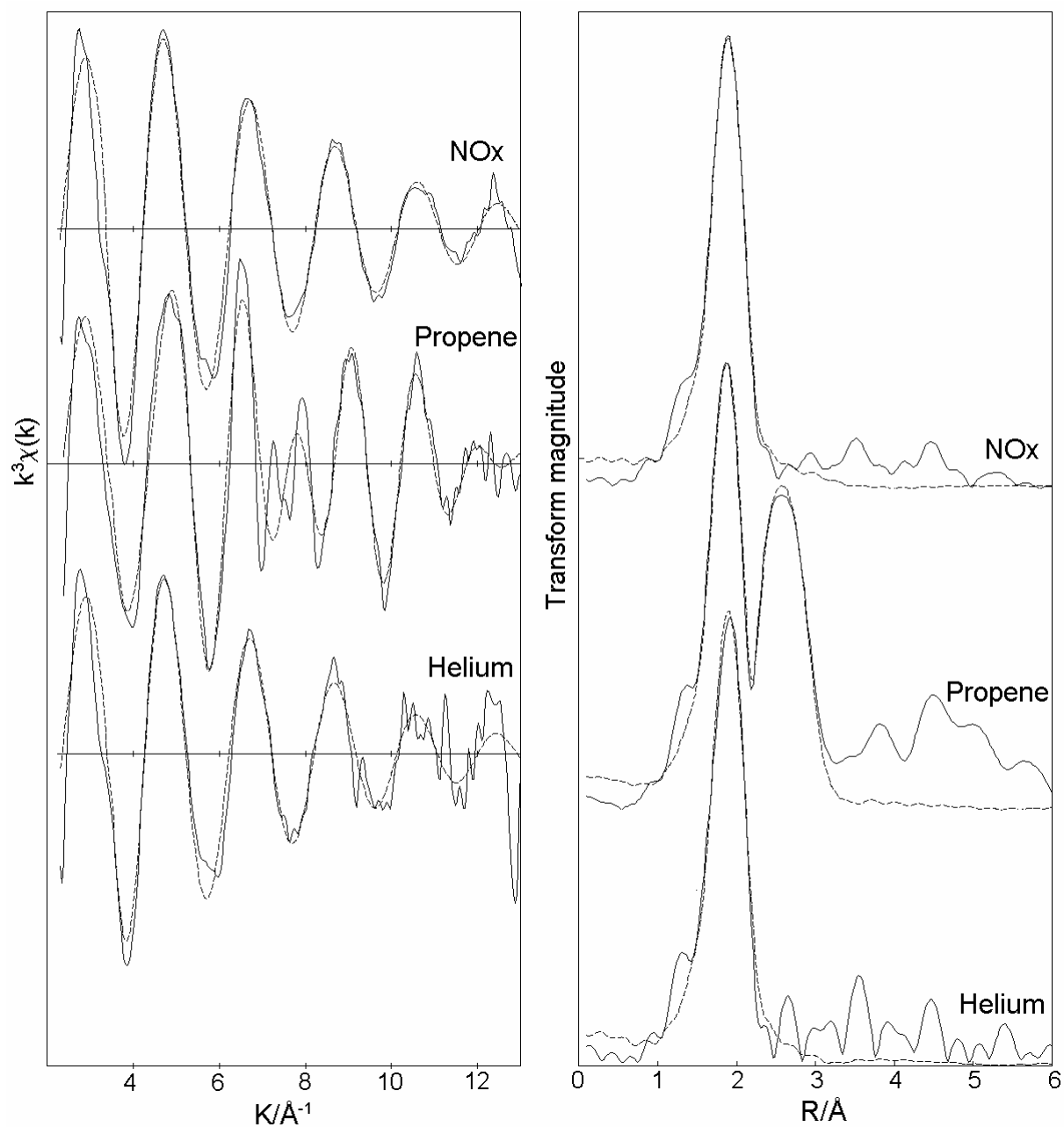


Figure 2 Experimental (—) and calculated (---) Fourier Filtered (1-25) k^3 -weighted EXAFS and its Fourier Transform for the low copper content CuSAPO-5 system; heated in helium, treated in propene and then NOx.

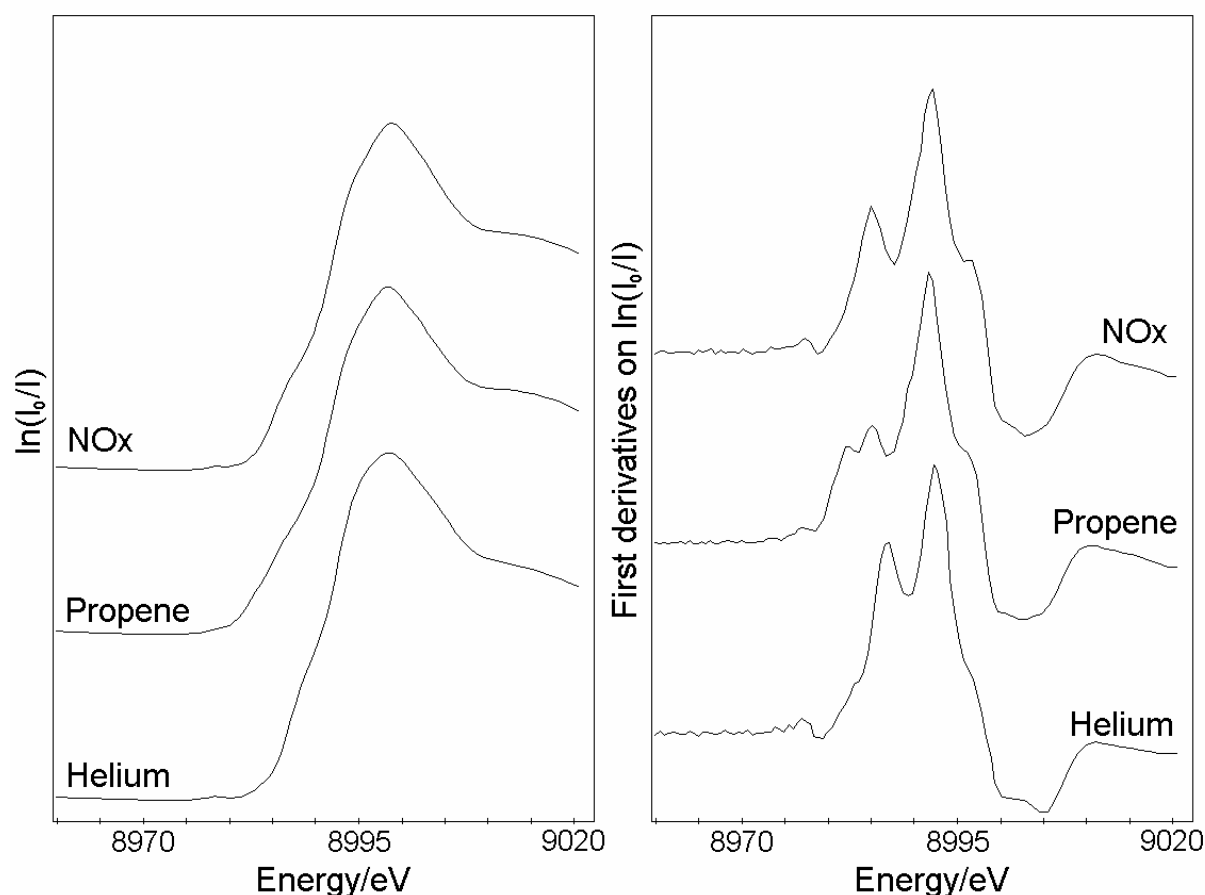


Figure 3 Normalised Cu K-edge XANES of the high copper content CuSAPO-5 system heated in helium, treated in propene and finally NOx.

In situ XAS studies on the different stages of the SCR process on the low copper content CuSAPO-5 show that to a small extent auto-reduction occurs on heating the catalyst in helium (Fig. 1 and 2). Propene treatment at 500 °C reduces copper(II) to copper(I) and metallic copper. The final treatment in NOx oxidises and redisperses the copper clusters and also oxidises copper(I) to copper(II). The redox behaviour of the copper valence state in CuSAPO-5 verifies this as the source of the mechanism for reducing NOx. Increasing the copper and silicon contents in the CuSAPO-5 system renders the material inactive for reducing NOx. This is attributed to the formation of copper(II) oxide which is inactive in the SCR process. From the XANES (Fig. 3) there appear to be only small changes to the copper environment, however, the EXAFS (Fig. 4) show that copper(II) oxide is formed in propene and further in NOx.

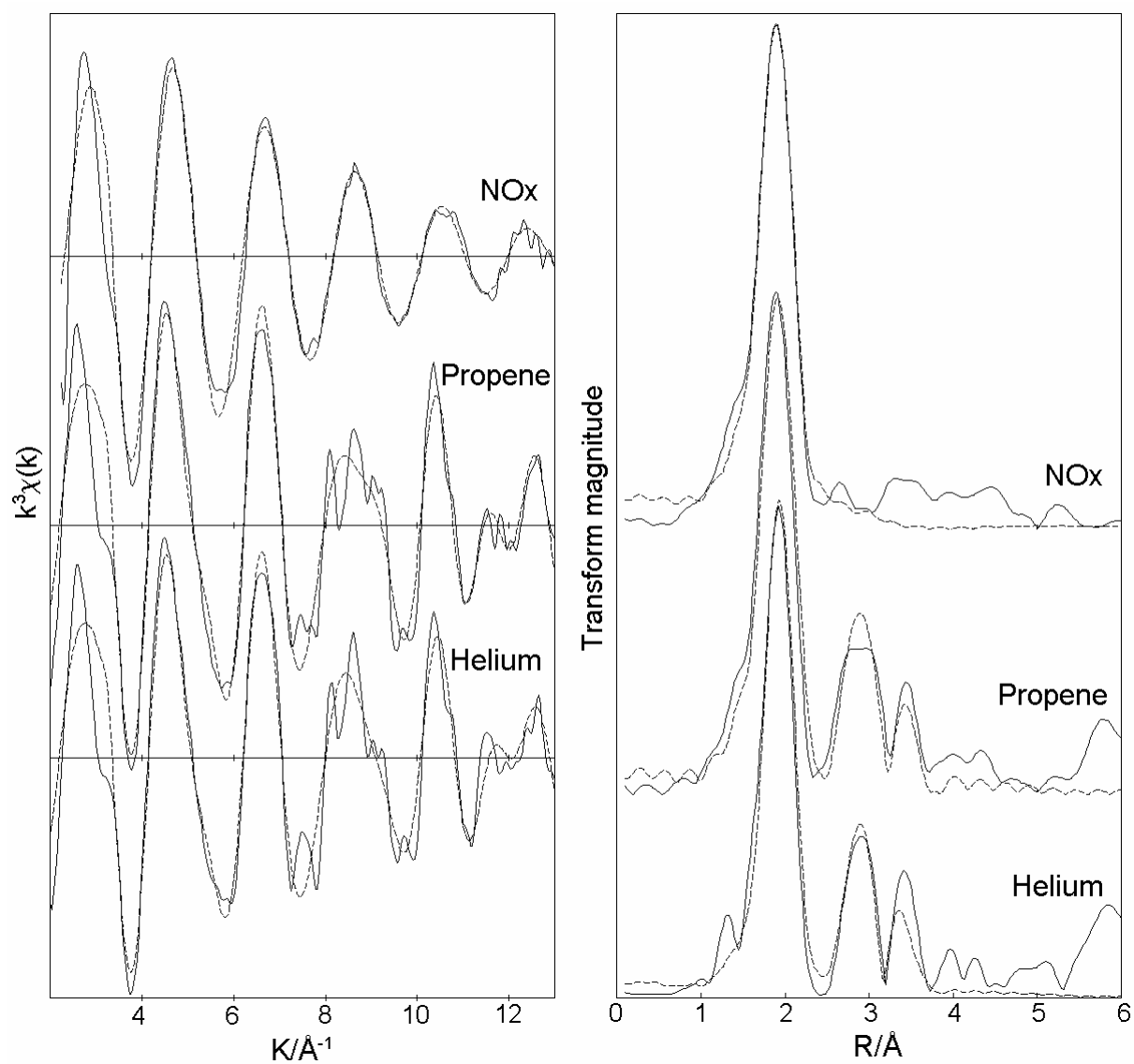


Figure 4 Experimental (—) and calculated (---) Fourier Filtered (1-25) k^3 -weighted EXAFS and its Fourier Transform for the high copper content CuSAPO-5 system; heated in helium, treated in propene and then NOx.

References

1. M. Iwamoto, H. Yahiro, Y. Mine, S. Kagawa, S. Chem. Lett., 1989, 213.
2. R. Burch and P. J. Millington, Appl. Catal. B: Env. 2 (1993) 101.
3. J. Valyon and W. H. Hall, J. Phys. Chem. 97 (1993) 1204.
4. D.-J. Liu and H. J. Robota, Appl. Chem. B: Env. 4 (1994) 155.