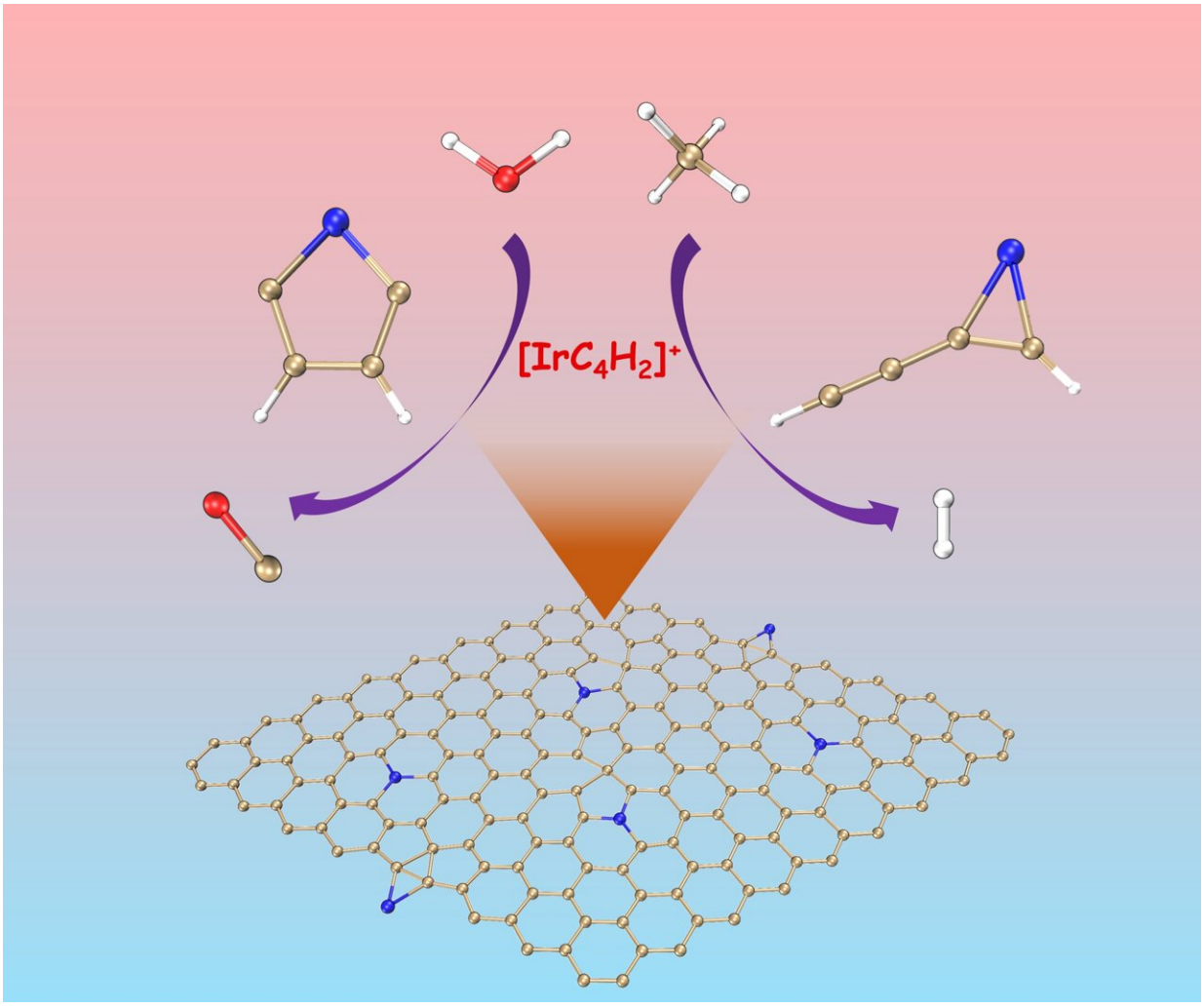
How two isomers of $[IrC_4H_2]^+$ independently react with either methane or water

September 20 2022



One of the two isomers of $[IrC_4H_2]^+$ only activates methane while the other is solely reactive with water to produce CO. Credit: Science China Press

This study was led by Prof. Shaodong Zhou (College of Chemical and Biological Engineering, Zhejiang University) and Prof. Xiao-Nan Wu (Department of Chemistry, Fudan University). The experiments were performed by using an ion trap mass spectrometer equipped with a laser vaporization–supersonic expansion ion combined with quantum chemical calculations.

Interestingly, under the employed conditions two isomers of $[IrC_4H_2]^+$ co-exist with different reactivities, one of them only activates methane while the other is solely reactive with water to produce CO. Apparently, upon varying the coordination patterns, the Ir center gains rather distinct capabilities of mediating the bond breaking and making processes. The reactivity toward methane mainly depends on the orbital orientation, while the π-aromaticity of the reaction complex matters for the conversion of water.

"Due to the complex surface structure and composition of catalysts, it is of great significance to correlate the electronic structure of the active center with its reactivities. As an ideal model to study the reaction mechanism at strictly a molecular level, gas-phase reaction can be carried out under the conditions excluding the interference of the external environment and, being well repeatable. Combined with quantum chemical calculation, it can help us understand deeply the reaction mechanism and implement the rational design of high-performance catalysts," Zhou says.

A few implications thus emerge for designing an Ir-catalysts for Steam reforming of methane: 1) more electron hole is expected on the d orbits (likely induced by local polarization) for the sake of the initial H_3C-H activation; 2) in the interaction of the Ir center with the CH_4/H_2O molecule, an increase of the local aromaticity disfavors further transformation, while an increase of the local anti-aromaticity is indicative for further bond activation; the increase of both the

aromaticity and anti-aromaticity may be more obvious for water.

The research was published in *Science China Chemistry*.

More information: Bowei Yuan et al, On the distinct reactivity of two isomers of [IrC4H2]+ toward methane and water, *Science China Chemistry* (2022). DOI: 10.1007/s11426-022-1342-4

Provided by Science China Press