Supporting Information

Design and Synthesis of Bi-functional Co-containing Zeolite ETS-10 Catalyst with High Activity in the Oxidative Coupling of Alkenes with Aldehydes for Preparing \(\alpha,\beta\)-Epoxy Ketones

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Fig. S1. TEM images of thin-sectioned Ni-METS-10 samples.
To examine the possible reaction mechanism, radical trapping experiment was performed. Typically, 50 mg catalysts, styrene (0.6 mmol), 2,2,6,6-tetramethyl-1-piperidinyl oxy (TEMPO, 1.2 mmol), benzaldehyde (1 mmol), CH$_3$CN (2.0 mL), and TBHP (1.2 mmol, 70 % aqueous solution) were put into the 10 mL reaction tube. After that, the reaction tube was put into oil bath with temperature of 80 °C. The pure product was obtained by flash column chromatography on silica gel. The structure of the obtained product was confirmed by $^1$H NMR and $^{13}$C NMR spectra. The result showed that TEMPO-adduct aldehyde 4 was the main product (Fig. 2). These results demonstrated that acyl radical was generated, which possibly originated from the abstraction of the aldehydic hydrogen by the alkyloxy radical under the reaction conditions.
**Fig. S3.** CO$_2$-TPD curves of Co-METS-10 and METS-10 samples  
(Experimental: The basicity of the supports and catalysts were measured by CO$_2$ temperature-programmed desorption (CO$_2$-TPD) on a Micromeritics ASAP2920 instrument. Typically, 300 mg of the sample were placed in a quartz tube and pretreated in a helium stream at 450 °C for 90 min. After the sample was cooled to 50 °C, CO$_2$ gas was flowed over the sample for 30 min. After removing the physically adsorbed CO$_2$ by flowing helium for 90 min at 50 °C, the sample was heated from 50 to 460 °C at a rate of 10 °C/min.).

**Discussion:**

The oxidative coupling of alkenes with aldehydes underwent radical reaction mechanism. The generation of alkylxy radical is crucial. Generally, the tert-butyl hydroperoxide can split into alkylxy radical under heating. Both of the basicity and metal can accelerate the formation of alkylxy radical. Professor Tang’s study result shows that the strong basic METS-10 catalyst facilitates the formation of alkylxy radical at relatively low temperature of 70 °C. Li and Ge’s groups reported that the TBHP also can be transformed into alkylxy radical over metal Fe and Co under high temperature (85-120 °C). In our case, at reaction temperature of 60 °C, METS-10 catalyst has higher activity than Co-METS-10, which could be attributed to that the density of basic sites on METS-10 is higher than on Co-METS-10 (**Fig. S3**). In contrast, when the reaction temperature rose to 70 and 80 °C, not only the basic sites but also the metal Co in the Co-METS-10 can simultaneously promote formation of more alkylxy radical spited from TBHP. Therefore, Co-METS-10 catalyst shows higher activity than METS-10 catalyst at the relatively high temperatures. In contrast, when the reaction temperature rose to 70 and 80 °C, not only the basic sites but also the metal Co in the Co-METS-10 can simultaneously promote formation of more alkylxy radical
spited from TBHP. Therefore, Co-METS-10 catalyst shows higher activity than METS-10 catalyst at the relatively high temperatures.