Lithium promotion of Pt/m-ZrO$_2$ for low temperature water-gas shift

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Abstract

The promoting role of lithium on Pt/m-ZrO$_2$ catalyst for low temperature water-gas shift (WGS) was investigated. Increasing Li loading to 0.54% facilitated formate C-H bond scission accelerating the WGS rate, while higher loadings blocked Pt hindering CO$_2$ desorption. Electronic and geometric structure of the catalysts were explored.

Background

Low temperature water-gas shift (LT-WGS) is an important catalytic step for the production of pure H$_2$ with the potential for use in PEM fuel cells for transportation and portable power, as well as in biomedical applications to decrease oxidative stress. In the mid- 2000s, Honda Research-USA, Inc. (HRI-USA) found that addition of Na to Pt/ZrO$_2$ significantly promoted the LT-WGS rate. Recently, we examined the type and loading effect of alkali dopants (Na, K, Rb, and Cs) to shed light on the nature of the alkali promoting effect. The general trend that has emerged may be explained based on a mechanism involving surface formates and carbonates in the pathway. In the early 1990s, Shido and Iwasawa proposed that the rate limited step of Rh/ceria , a related catalyst, involved C-H bond scission of formate. Later, a Pt loading investigation by the Davis group suggested that this mechanism likely occurs at the interface between the metal and the support. The current collaboration has shown that the loading of Na is critically important - too low and the electronic modification does not occur; too high and Pt sites responsible for facilitating CO$_2$ removal become blocked and the catalyst becomes too basic. While an optimized loading of K was also found to promote WGS albeit less effectively than Na, Rb [6a] and Cs [6b] were the most effective in promoting the forward formate decomposition in steam but the overall WGS rate was decreased. This was due to excessive basicity preventing liberation of CO$_2$. In the current investigation, we examine the effectiveness of Li as a promoter. While formate C-H bond weakening was examined by in-situ DRIFTS, electronic structure was investigated by XANES, and particle size was obtained by EXAFS. Catalytic tests were performed using a fixed bed reactor.

Material and Methods

Alfa Aesar monoclinic ZrO$_2$ pellets were ground and sieved to 63 - 150 μm. Tetraammine platinum(II) nitrate and lithium nitrate served as precursors and were added sequentially by incipient wetness impregnation (Pt first, Li second, with intermediary drying and calcination). Catalysts were characterized by BET surface area, TPR, TPR-MS, in-situ DRIFTS of adsorbed CO and formate decomposition, TPD-MS of formate decomposition, and EXAFS/XANES, and tested using a fixed bed reactor.
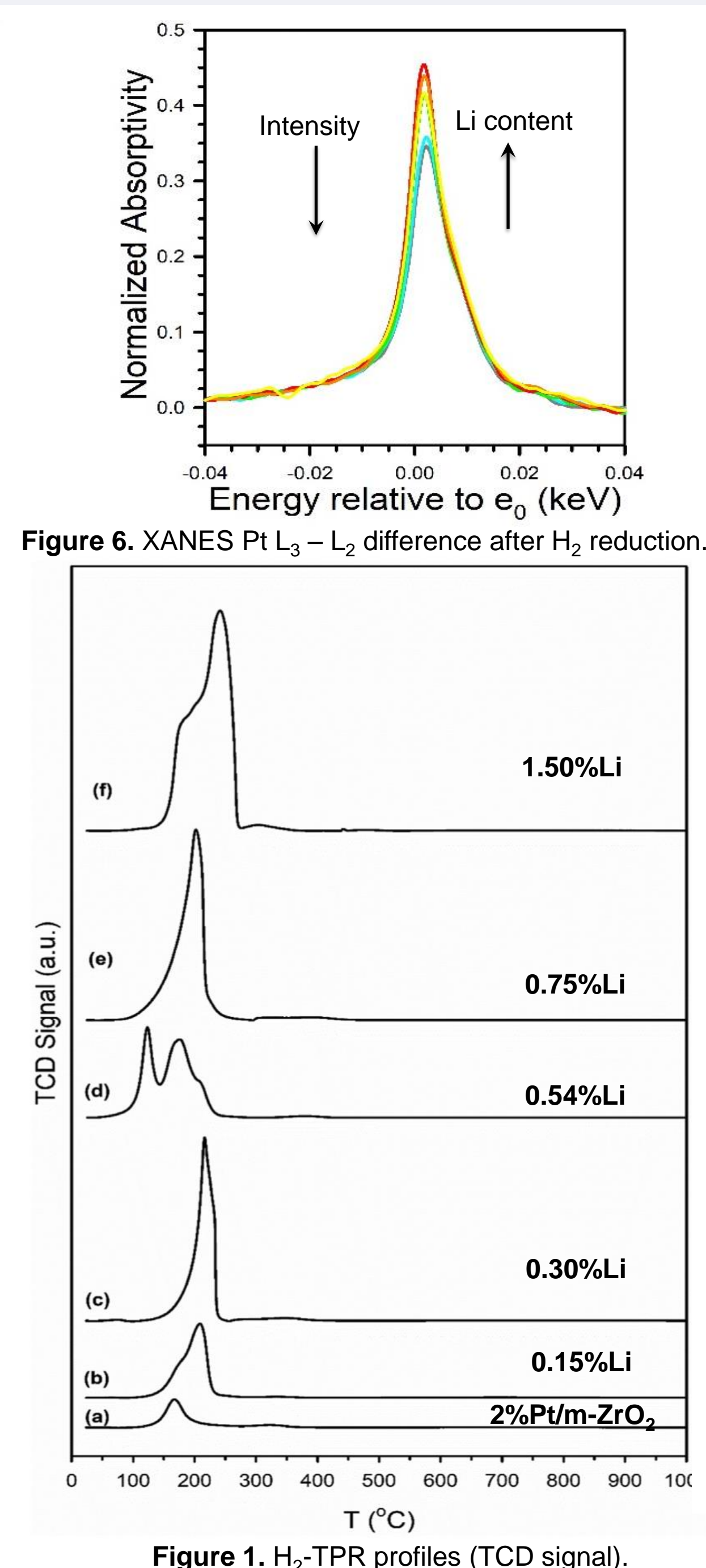
Results

Figure 6. XANES Pt L$_3$ – L$_2$ difference after H$_2$ reduction.

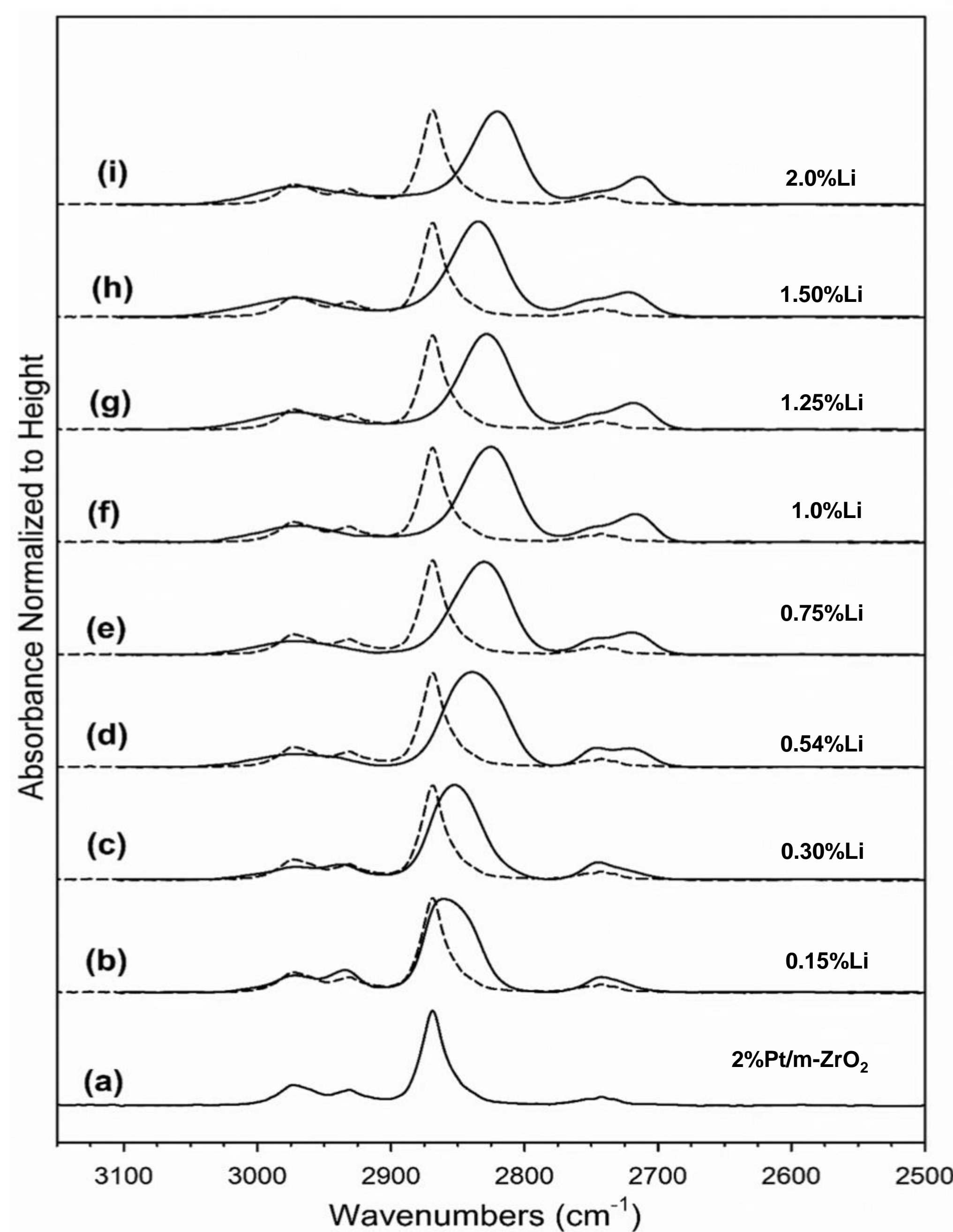Figure 1. H$_2$-TPR profiles (TCD signal).

Figure 2. Formate ν(CH) band intensity for DRIFTS of adsorbed CO. Dashed line represents the 2%Pt/m-ZrO$_2$ reference catalyst.
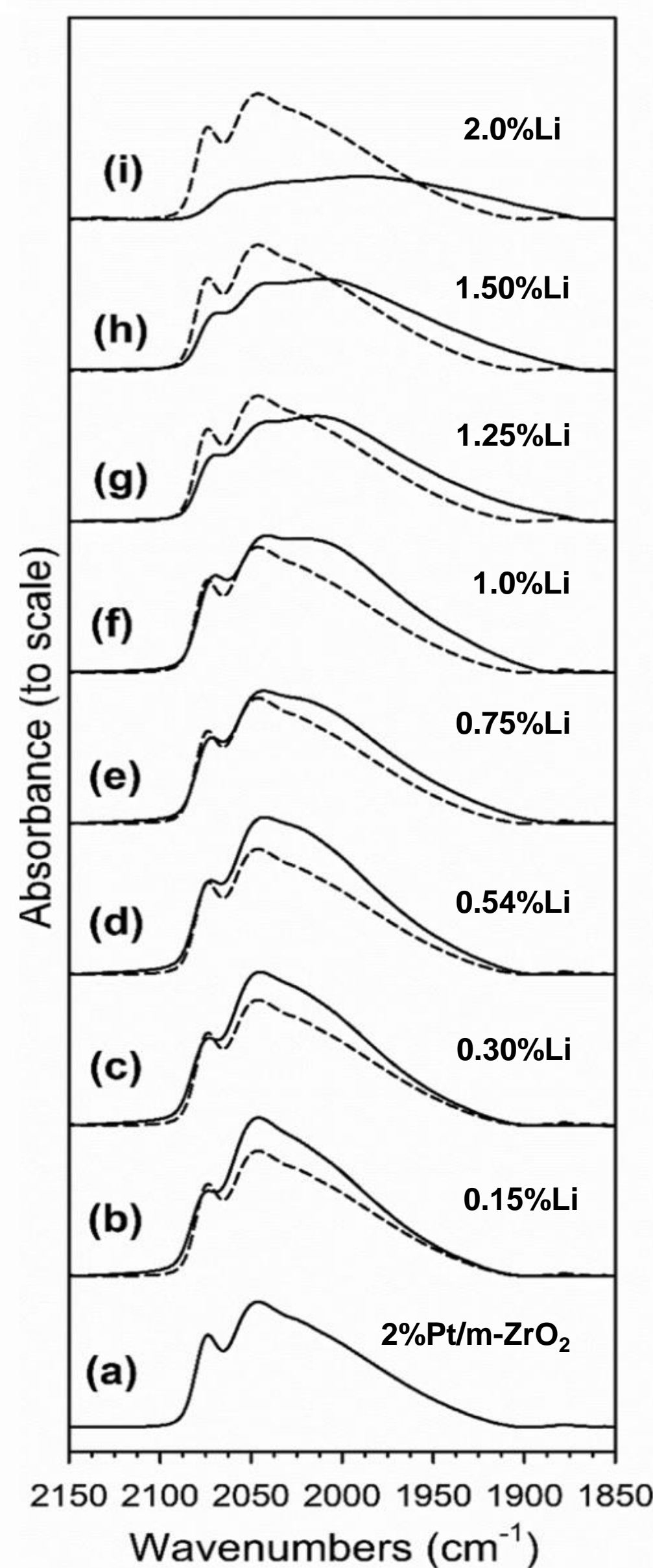

Figure 3. DRIFTS ν(CO) band intensity for Pt carbonyl from adsorbed CO. Dashed line represents the 2%Pt/m-ZrO$_2$ reference catalyst.
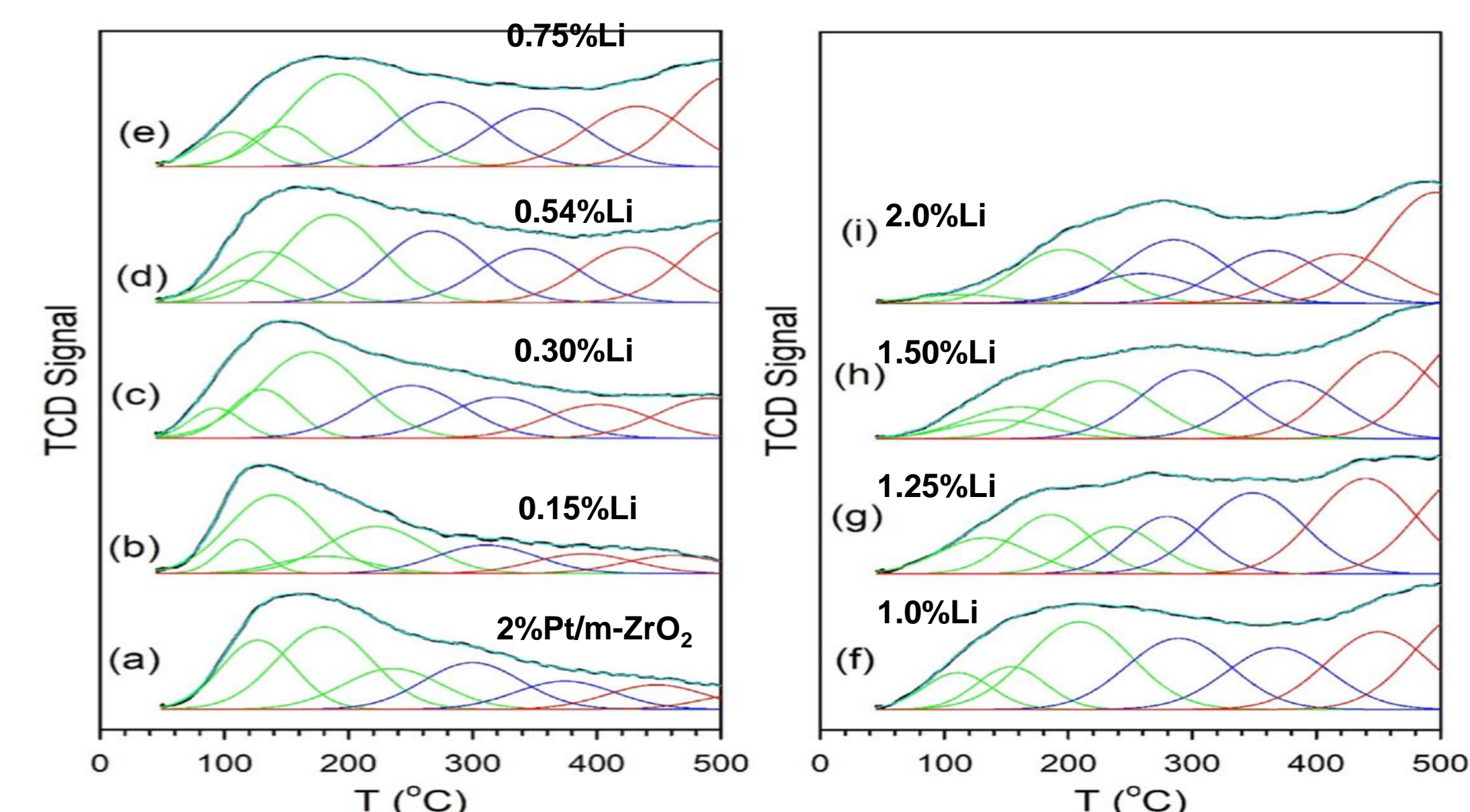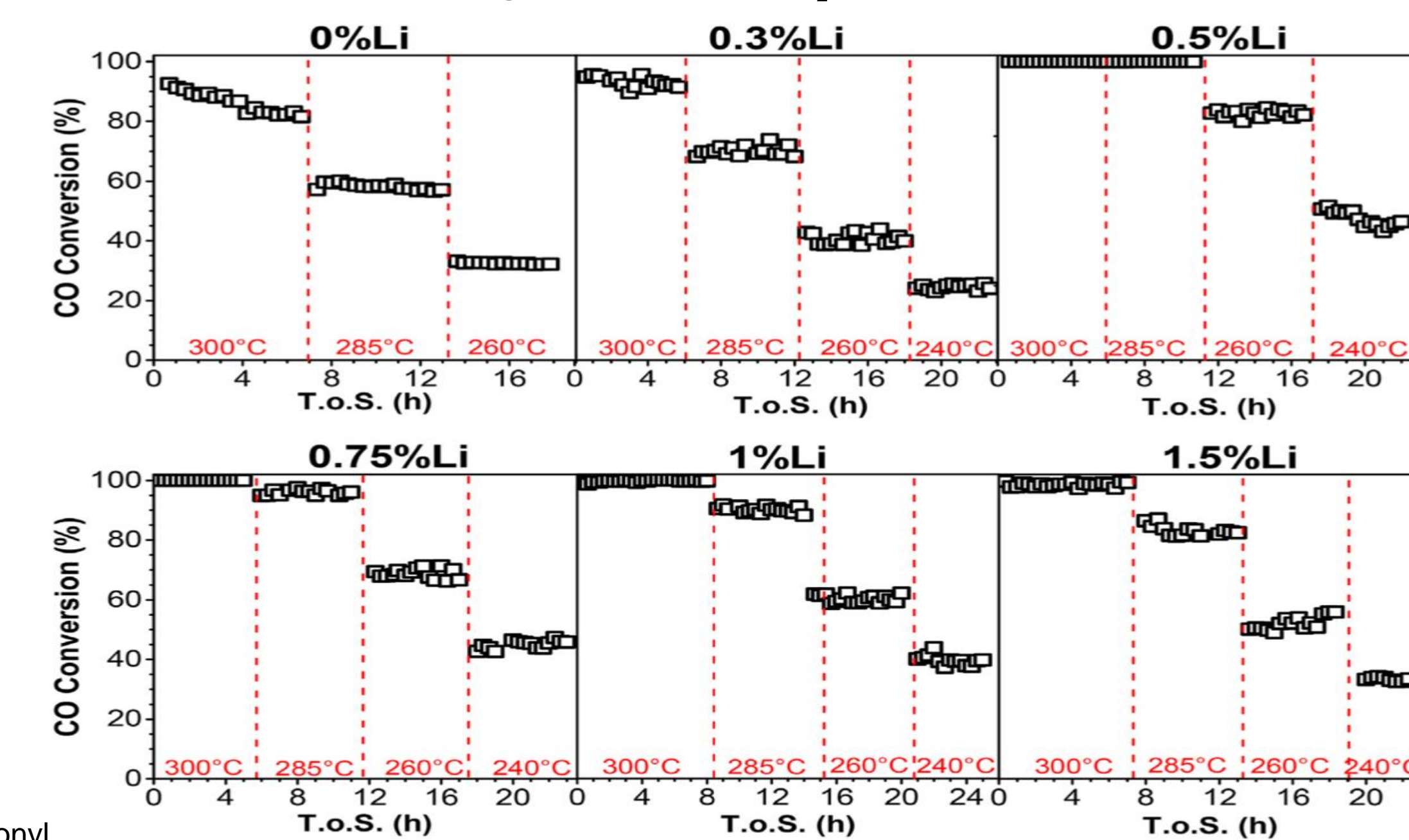

Figure 4. TPD-MS of CO$_2$ desorption.

Figure 5. X_{CO} vs. time on stream during LTS for the prepared catalysts (26.1%H$_2$O, 2.9%CO, 29.9%H$_2$, 27.8%N$_2$, balance He, P 1atm, SV 167,638 Ncc/h·g$_{cat}$).

Figure 1 shows the H$_2$ reduction profiles, which involve reduction of Pt oxide, dissociation and spillover of hydrogen to the m-ZrO$_2$ surface to form bridging OH groups, and decomposition of surface carbonate. Increasing Li content increases catalyst basicity resulting in more adsorbed surface carbonate. **Figure 2** shows that as the Li loading is increased, there is a more significant C-H bond weakening of formate, and the ν(CH) band systematically shifts from 2868 (unpromoted) to 2820 cm^{-1} (with 2% Li). At the same time, the Pt site capacity gradually diminishes with Li addition, as shown in **Figure 3** . This hinders product CO$_2$ desorption. **Figure 4** CO$_2$ TPD profiles show that with increasing Li content, higher catalyst basicity and the blocking of Pt sites by Li hinders carbonate decomposition. As depicted in **Figure 5**, The WGS rate is accelerated up to 0.5%Li addition, and then it gradually diminishes at higher loadings. This loading is similar atomically to the Na dopant level that achieved optimum promotion (1.8 - 2.5%Na) of 2%Pt/ZrO$_2$ in previous work. In XANES Pt L$_3$ – L$_2$ difference spectra (**Figure 6**), no evidence of e$^-$ transfer from Li to Pt nanoparticles (~0.8 - 1 nm) was found [5].

Summary

Increasing the loading of lithium dopant had a remarkable positive effect on the LTS rate up to 0.54% lithium; although the catalysts tested up to 1.5%Li had better activity as compared to the unpromoted 2%Pt/m-ZrO$_2$ catalyst, additional increases in lithium loading beyond 0.54%Li decreased the rate. CO$_2$ temperature programmed desorption measurements also showed that high levels of lithium increased catalyst basicity. Thus, an excessive Li loading tended to inhibit desorption of product CO$_2$, an acidic molecule the removal of which is metal-catalyzed. In-situ DRIFTS shed light on both promoting and inhibiting effects of Li as a function of lithium loading: (1) at all loadings, Li weakens the C-H bond of formate, and this bond breaking is the proposed rate limiting step of the interfacial surface formate mechanism; and (2) at levels of lithium above 0.54%Li, the platinum site capacity, which is needed for Pt-catalyzed hydrogen transfer and CO$_2$ desorption steps, becomes increasingly blocked by Li.

Acknowledgments

References

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