Effect of gallium as an additive on activated carbon-supported cobalt catalysts for synthesis of higher alcohols by CO hydrogenation

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Abstract: In this work, we report a gallium modified Co/AC catalyst (Ga–Co/AC) which is capable to improve the selectivity of alcohols (S_{ROH}) from CO hydrogenation. The characteristic studies revealed that the addition of Ga could elevate the reduction temperature of Co_3O_4 and modulate the surface distribution of Co^0 and Co^{2+}. The dual active sites of Co^0–Co^{2+} were responsible for the formation of alcohols and the improved S_{ROH} could be assigned to the moderate ratio of $Co^{2+}/(Co^0 + Co^{2+})$. The finding indicates that the Ga–Co/AC would be an effective catalyst for the synthesis of higher alcohols by CO hydrogenation.

Keyword: Synthesis of higher alcohols, gallium doping, Co^{2+}–Co^0 dual active sites.

1. Introduction

Synthesis of higher alcohols from syngas has attracted extensive attention due to the wide applications as fuel, fuel additives and chemicals[1]. The traditional Co-based catalysts represent a relatively high active for CO conversion and a compromised ability for carbon length growth. However, Co-based catalysts generally produce minor amount of oxygenates in typical reaction condition. Many methods have been developed to improve the selectivity of alcohols (S_{ROH}), for example, the addition of promoters and selection proper supports. Herein, we prepare a Ga doped Co/AC catalyst (Ga–Ca/AC) for the synthesis of higher alcohols. The results indicate that the Ga–Co/AC can be a kind of new catalyst which presents higher selectivity to the C_{2+} alcohols (C_{2+}–OH). The catalyst structure and the relationship between the catalyst structure and catalytic performance are then addressed by a series of spectroscopic studies.

2. Experiment

The supported Ga–Co catalysts were prepared by a conventional incipient wetness co-impregnation method. The impregnated samples were dried at 100 °C and calcined at 350 °C for 5 h in a flow of Ar. The Co loading was kept at 15 wt% and the content of Ga was varied from 0 to 3.0 wt%(labeled as x; x = 1.5, 2.0, 2.5, and 3.0 wt%). The reaction was performed at a home-made fixed-bed reactor under 220 °C, 3.0 MPa, 4000 mL/(g·h). The catalytic data were collected at a steady state.

3. Results and Discussion

The TPR profiles for several catalysts are shown in Figure 1A. As shown in Figure 1A, the intensity of the second peak was obviously decreased after the addition of Ga. It suggested that the doping of Ga hindered the reduction of CoO. The Co 2p XPS profiles for all reduced catalysts are illustrated in Figure 1B. As shown in Figure 1B, the Co^0 and Co^{2+} species simultaneously existed. It could also be seen that the intensity of Co^{2+} peaks increased while Ga was introduced. It suggested that the addition of Ga was able to modulate the distribution of surface Co species and elevate the ratio of $Co^{2+}/(Co^{2+} + Co^0)$.

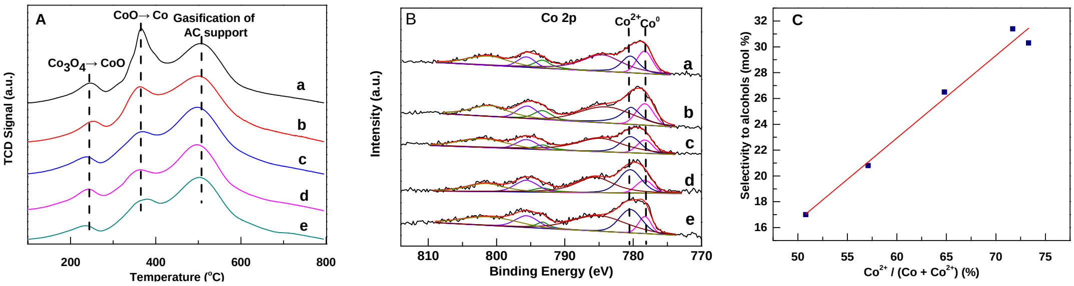

Figure 1. (A) H_2-TPR profiles of 15Co–*x*Ga/AC, (B) Co 2p XPS profiles of 15Co–*x*Ga/AC and (C) Relationship between ratio of $Co^{2+}/(Co^0 + Co^{2+})$ and selectivity of alcohols over 15Co–*x*Ga/AC. (a) 15Co/AC, (b) 15Co–1.5Ga/AC, (c) 15–2.0Ga/AC, (d) 15Co–2.5Ga/AC, and (e) 15Co–3.0Ga/AC.

The catalytic performance is summarized in Table 1. As shown in Table 1, the conversion decreased after the addition of Ga. It could be ascribed to the decreasing of available metallic Co active sites which were related to the dispersion and reduction of Co species. According to characterization results, the introduction of Ga improved the Co dispersion but hindered its reduction. The addition of Ga suppressed the CO conversion but significantly improved S_{ROH}. Figure 1C displays the selectivity of alcohols as a function of $Co^{2+}/(Co^{2+} + Co^0)$ ratio. As Figure 1C shown, a linear correlation between the S_{ROH} and the ratio of $Co^{2+}/(Co^{2+} + Co^0)$ could be found. Previous works reported that the dual active sites of Co^{2+}–Co^0 were responsible for the synthesis of alcohols[2] and Co^{2+} favored the formation of alcohols[3]. Therefore, the promotional effects of Ga on S_{ROH} could be assigned to the moderate ratio of $Co^{2+}/(Co^{2+} + Co^0)$ and the combination of Co^{2+}–Co^0 was considered as the active sites for the production of alcohols.

Table 1 Catalytic performance of 15Co-*x*Ga/AC catalysts

Catalyst	Conversion	Selectivity (mol%)			Distribution of alcohols (mol%)		
	(mol%)	ROH	RH	CO_2	CH_3OH	$C_{2\text{-}5}$–OH	C_{6+}–OH
15Co/AC	25.9	17.0	81.5	0.5	11.0	43.4	45.6
15Co–1.5Ga/AC	28.9	20.8	78.4	0.8	15.7	48.9	35.4
15Co–2.0Ga/AC	21.8	26.5	73.0	0.5	19.8	40.3	39.9
15Co–2.5Ga/AC	13.1	30.3	68.7	1.0	19.2	56.3	24.5
15Co–3.0Ga/AC	10.6	31.4	66.4	2.2	15.6	58.4	26.0

4. Conclusions

In summary, the addition of Ga to Co/AC by the conventional co-impregnation method followed by controlled reduction can prepare an effective catalyst for the synthesis of higher alcohols by CO hydrogenation. The S_{ROH} is increased from 17.0 % over 15Co/AC to 31.4 % over the optimized 15Co–3.0Ga/AC. The presence of Ga is able to modulate the distribution of surface Co species and the ratio of $Co^{2+}/(Co^{2+} + Co^0)$. The enhanced selectivity to higher alcohols is ascribed to the moderate ratio of $Co^{2+}/(Co^{2+} + Co^0)$ and the dual active sites of Co^{2+}–Co^0 are responsible for the synthesis of alcohols.

References

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