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Metallic Aluminum Content in Catalysts

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Abstract: Water is an inevitable by-product of Fischer–Tropsch synthesis (FTS). Accumulation of water in the reaction medium can lead to oxidation and sintering of cobalt particles and reduce catalyst lifetime. This study investigates the influence of incorporating zeolites with different cationic forms into cobalt-based FTS catalysts and examines how the hydrophilicity/hydrophobicity of the zeolite–water interface affects catalyst performance. Metallic aluminum content in catalysts was monitored before and after 120 hours of FTS. Results show that H-form zeolites protect metallic aluminum from oxidation due to competitive adsorption of hydrocarbons, whereas hydrophilic zeolites allow greater oxidation. The findings indicate that selecting appropriate zeolites can control interfacial hydrophobicity, minimize metal oxidation, and influence the composition of synthetic crude oil products.

Keywords: Fischer–Tropsch Synthesis, Cobalt Catalyst, Zeolite, Hydrophilicity, Hydrophobicity, Metallic Aluminum, Catalyst Deactivation, Synthetic Crude Oil

Introduction

Water is an inherent by-product of Fischer–Tropsch synthesis (FTS). Accumulation of water in the reaction medium leads to oxidation and sintering of active metal particles (Co), which can result in rapid catalyst deactivation. One approach to mitigating the negative effects of water in FTS is to regulate the hydrophilicity/hydrophobicity of the catalyst–product interfacial surface. Zeolites can be classified as hydrophilic or hydrophobic based on their ability to adsorb water from hydrocarbon–water mixtures. [1][2]

Methodology

Hydrophilic zeolites typically contain high amounts of alkali and alkaline-earth metals and have an affinity for polar molecules small enough to enter their pores. High-silica zeolites, on the other hand, are generally hydrophobic and preferentially adsorb hydrocarbons from water–hydrocarbon mixtures.[3][4]

Results

Table 1 presents the metallic aluminum content of the tested catalysts before and after 120 hours of synthesis. Interestingly, in the case of zeolite-free comparison catalysts, approximately 60% of metallic aluminum was oxidized under synthesis conditions, regardless of preparation method. In contrast, metallic aluminum in all cation-exchanged zeolites was oxidized to varying degrees, with no clear correlation to either the cation type or preparation method. Notably, metallic aluminum in the mixed catalyst based on KA was most heavily oxidized (up to 72%) under synthesis conditions.[5][6]

Table 1. Metallic Aluminum Content in Catalysts

Catalyst	**Al_met, wt.%**		**%**
	Before synthesis	After synthesis	
	Impregnated catalysts		
Co/Al_2O_3	27	11	59
Co/CaA	33	18	45
Co/NaX	29	10	66
Co/HY_6	27	24	11
Co/HY_{30}	26	20	23
Co/HB	25	22	12
	Mixing catalysts		
$Co\text{-}Al_2O_3$	38	14	63
Co-KA	39	11	72
Co-CaA	40	19	52
Co-NaX	38	21	45
Co-HY6	37	28	24
$Co\text{-}HY_{30}$	38	36	5
Co-HB	37	35	5

In H-form zeolite-based catalysts, regardless of the cobalt incorporation method, the metallic aluminum content decreased significantly less during synthesis: HY6-based catalysts showed a 11–24% decrease, HY30-based catalysts a 5–23% decrease, and HB-based catalysts a 5–12% decrease.[7]

As shown in Table 1, H-form zeolites inhibit the oxidation of metallic aluminum in the composite, likely due to competitive adsorption of hydrocarbons and water on the zeolite. This work discusses competitive sorption of water and hydrocarbons by zeolites in hydrocarbon–water mixtures. According to the classification in [8], high-modulus H-form zeolites are considered hydrophobic (oleophilic), whereas FAU- and LTA-type zeolites in cation-exchanged forms (alkali or alkaline-earth metals) are hydrophilic (oleophobic). It can be assumed that in the presence of oleophilic H-form zeolites, a film of hydrocarbons formed on the surface protects the catalyst from water vapor and metallic aluminum oxidation.

Thus, incorporating an oleophilic zeolite into an FTS catalyst can prevent the oxidative effects of synthesis water on the active cobalt-containing surface, reducing both metal oxidation and metal–support interactions [9]. This may extend catalyst lifetime without loss of activity or selectivity [10].

Discussion

Moreover, high-silica H-form zeolites can generate additional Brønsted acid sites in the presence of water molecules [11]. This explains differences in product composition observed with HB- and HY30-based catalysts, as hydrocarbon transformations in FTS occur primarily on Brønsted sites of zeolites (Figure 1).[12][13]

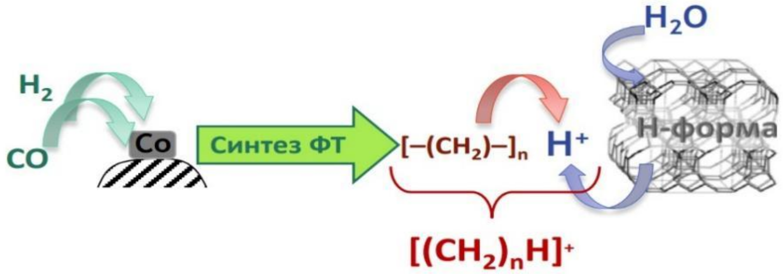

Figure 1. Schematic representation of FTS water interaction in the presence of HB zeolite

Conclusion

In summary, using zeolites in composite cobalt catalysts allows control over the hydrophilicity/hydrophobicity of the catalyst–product interface and can influence the composition of synthetic crude oil.[14]

Water produced during FTS leads to cobalt oxidation and potential catalyst deactivation; regulating catalyst hydrophilicity/hydrophobicity is essential to mitigate this effect. H-form zeolites incorporated into cobalt catalysts effectively protect metallic aluminum and active cobalt sites by competitive adsorption of hydrocarbons, thereby reducing oxidation. Hydrophilic zeolites or catalysts without zeolites show significantly higher metallic aluminum oxidation under the same synthesis conditions. The hydrophobicity of the zeolite influences the composition of the FTS products, including the selectivity of synthetic crude oil. Using oleophilic H-form zeolites in composite cobalt catalysts can extend catalyst lifetime without compromising activity or selectivity, making it a promising strategy for improved FTS catalyst design.[15]

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