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CO hydrogenation on group VI metal–ceria catalysts

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ABSTRACT

Ceria-supported chromium, molybdenum, and tungsten catalysts were prepared by impregnation. The prepared catalysts were characterized using N_2 adsorption, X-ray diffraction (XRD), the temperature-programmed reduction (H_2-TPR), and X-ray photoelectron spectroscopy (XPS) measurements. The catalytic activity in CO hydrogenation was evaluated using a fixed-bed pressurized flow reaction system under the following conditions: 260–300 °C, 5.0 MPa, GHSV of 5000 h^{-1}, and a H_2/CO ratio of 1.0–2.0. The effects of ceria support, group VI metals, and catalyst activation methods on C_{2+} alcohol synthesis were investigated. The use of ceria supports resulted in a decrease in the selectivity for CO_2, and in increases in the selectivity for C_{2+} alcohols and CO conversion. The selectivity for alcohols on the Mo-based catalysts was higher than those on the corresponding Cr or W-based catalysts. A comparison of the methods of activation for the $K_{005}Co_{06}$20MoCe catalyst demonstrated that sulfidation produced the highest CO conversion and selectivity for C_{2+} alcohols, as well as the lowest, hydrocarbon selectivity. XPS and H_2-TPR measurements show that the mixed metal sulfide phases, e.g., the Co–Mo–S phase, and the thiol group on the catalysts enhanced the formation of C_{2+} alcohols.

1. Introduction

Alcohols with more than two carbons, described as C_{2+} alcohols or mixed alcohols, are extensively utilized as chemical intermediates, such as plastics, solvents, paint, and aromatics, as well as alternative fuel. The demands for C_{2+} alcohols are increasing year by year. Currently, C_{2+} alcohols are synthesized by hydration or hydroformylation of olefins, which are derived from fossil resources [1]. Recently, it has become necessary to manufacture C_{2+} alcohols from sources other than fossil resources. Because the biomass wastes or residues can be used as feedstock for the production of C_{2+} alcohols via gasification to syngas, which is a mixture of hydrogen and carbon monoxide, the manufacture of C_{2+} alcohols does not need to rely solely on fossil resources. Therefore, considerable attention has been focused on the process of transforming syngas to mixed alcohols [2,3].

Noble metals, such as rhodium, exhibit good catalyst performance with their selectivity for C_{2+} alcohols [4,5]. However, these catalysts are sensitive to sulfur poisoning [6]. Thus, from a cost perspective, it is essential to explore non-noble metal catalysts for alcohol synthesis applications. Molybdenum-based catalysts are considered a promising candidate for the synthesis of mixed alcohols [2,3,7–9]. It is well known that the addition of transition metals, such as cobalt, as promoters to sulfided Mo/Al_2O_3 or MoS_2 drastically improves hydrodesulfurization (HDS) activity, and that WS_2 or Cr_2S_3-based catalysts have similar activity to those of MoS_2-based catalysts [10–13]. The addition of a transition metal to catalysts based on group VI metals also has the potential to promote the synthesis of mixed alcohols, e.g., by improving the propagation of carbon chains. This potential comes from the fact that transition metals, such as Fe, Co, and Ni, are also used as catalysts for F–T synthesis. The addition of group VIII metals, especially cobalt, on unsupported alkali–MoS_2 catalysts was reported to shift the selectivity for methanol toward C_{2+} alcohols and to decrease the selectivity for hydrocarbons [14]. Similar effects of adding cobalt were also shown in our previous study [7]. Therefore, alkali and Co-doped catalysts based on group VI metals could be expected to produce more C_{2+} alcohols.

In our previous study, we investigated the effects of acidity on catalysts during the synthesis of mixed alcohols [7]. Lower amounts of acid and an appropriate loading of K on the catalysts promoted the formation of C_{2+} alcohols. Ceria, which is a basic oxide, is available as a catalyst support for the exhaust-gas treatment of diesel engines and the steam reforming reaction, and it is known as a reducing agent [15,16]. It was also reported that ceria supports possessed reducibility and a redox equilibrium with Cu ($Ce^{4+} + Cu^0 \Leftrightarrow Ce^{3+} + Cu^+$) in the synthesis of C_{2+} alcohols over $CsCuCeO_2$ catalysts [17]. Because MoS_2-based catalysts possess the relatively high activity necessary for water–gas-shift reactions, they can readily form CO_2 [3,9]. It was proposed that CO_2 is formed via the surface catalytic reaction of the non-dissociatively adsorbed CO species, or CO molecule, with O* species derived from dissociatively adsorbed C–O species [3,7,18]. Therefore, it is likely that a ceria support could accept the dissociated oxygen species, and the formation of CO_2 might be suppressed on ceria-supported catalysts.

The influence of group VI metals on catalysts with a ceria support has not been elucidated with regard to the synthesis of C_{2+} alcohols. Thus, to elucidate those effects in the present study, we focused on

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evaluating the abilities of various K–Co-group-VI–metal–ceria catalysts to synthesize C_{2+} alcohols. A series of catalysts with ceria supports were prepared by impregnation, and the roles of ceria and the catalyst activation methods were investigated.

2. Experimental

2.1. Materials

Ceria in power form (Daiichi Kigenso Kagaku Kogyo Co., Japan) and SiO_2 (Japan Oil Co.) were purchased and used as supports. For preparation, commercial GR grade hexaammonium heptamolybdate 4-hydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), and potassium precursors: potassium nitrate (KNO_3) or potassium carbonate (K_2CO_3) (Wako Pure Chemicals, Japan, respectively), were used, and commercial 1 grade ammonium tungstate para pentahydrate ($(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ (88.0%)) was used. The feed gas was a mixture of a standard mix of $H_2/CO/N_2$ (45/45/10 vol.%) and hydrogen (purity: 99.999 vol.%).

2.2. Preparation of catalysts

All catalysts were prepared by the conventional and sequential impregnation procedure according to our previous study [7]. Ceria or SiO_2 support was impregnated with aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, or $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ as group VI metal precursors firstly, and was evaporated to dryness. Next, the aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ was introduced successively. The impregnated samples were pressurized for shaping under 60 MPa for 5 min and then pulverized to 20–80 mesh. After calcining in air at 450 °C for 12 h, the Co–group VI metal oxide precursor was impregnated with a solution of K_2CO_3 or KNO_3, being evaporated to dryness, and calcined in air at 450 °C for 12 h in the same way. The loading amounts of K_2O (or K_2CO_3), CoO, and group VI metal oxides are listed in Table 1. For investigation of the effects of group VI metals, the ratio of group VI metal to ceria support was constant at 0.23 (mol/mol). The prepared samples were denoted as K_xCo_yzMCe (x: molar ratio of K/M; y: molar ratio of Co/M; z: weight of group VI metal (wt.%); M: group VI metal (Cr, Mo, or W), abbreviation to parenthetic C in the case of K_2CO_3, and only "K" in the case of KNO_3). All catalysts were pretreated according to one of three procedures. In the sulfidation procedure, all samples were sulfided in situ with a mixed gas of 5 vol.% H_2S and 95 vol.% H_2 at a flow rate of 30 ml/min at 400 °C at temperature ramp rate of 5 °C/min and atmospheric pressure for 3 h. For reduction of the $K_{005}Co_{06}$20MoCe sample, hydrogen (purity of 99.999 vol.%) was substituted for a mixed gas of H_2S/H_2 at the same flow rate, pretreatment temperature and temperature rate, and time as those used for sulfidation. The $K_{005}Co_{06}$20MoCe sample was also pre-sulfided at 400 °C for 3 h and was then reduced at 320 °C for 3 h to investigate the effects of the catalyst activation methods.

2.3. Characterization of catalysts

The specific surface area and pore size of all samples were determined using N_2 adsorption with an automatic specific surface area and pore volume measurement device (BELSORP-mini II, BEL Japan) [19]. X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer (RAD-IIC, Rigaku Co.) with Cu Kα radiation. A continuous scan mode was used to collect 2θ data from 5° to 80° at the rate of 1.5°/min. The voltage and current were 40 kV and 30 mA, respectively. The reducibility of the sulfided catalysts was measured with the temperature-programmed reduction (H_2-TPR) using a ChemBET Pulsar TPR/TPD instrument (Quantachrome Instruments). Before H_2-TPR measurements, several samples (0.1 g) were pretreated as described above in Section 2.2. H_2-TPR analyses were performed by a previously published method [7]. H_2S molecules, which were adsorbed from sulfided samples, were trapped with grained Fe_2O_3 as adsorbent. Prior to X-ray photoelectron spectroscopy (XPS) analyses, all samples were pretreated in a quartz reactor. The XPS measurements of the catalysts were taken using a Shimadzu ESCA 3200 photoelectron spectrometer equipped with a magnesium source (Mg Kα = 1253.6 eV) that was operated at 8 kV and 30 mA under previously published conditions [20]. The envelopes of Mo 3d, Co 2p, S 2p, K 2p, O 1 s, C 1 s, and Ce 3d were measured and those spectra were deconvoluted with a curve-fitting based on a Gaussian function.

2.4. CO hydrogenation and analysis

Prior to activity tests, all catalysts were pretreated as described above in Section 2.2. The tests for alcohol synthesis from syngas were performed using a fixed-bed pressurized flow reaction system with a micro-reactor of conventional design. The detailed experimental procedures and sampling methods followed those of a previously published source [7]. The reaction conditions were 260–300 °C, 5.0 MPa, gas hourly space velocity (GHSV) of 5000 h^{-1}, and H_2/CO ratio of 1.0 or 2.0. An online gas chromatograph was equipped with FID (Model GC-14B, Shimadzu; CP-Sill 5CB, 0.25 mm × 60 m length) to analyze any oxygenated compounds produced, such as alcohols and hydrocarbons. The oxygenated compounds as esters were not detected regarding all samples under the detectable analysis condition. Another online GC–TCD (Unibeads C, 1/8 in. × 2.0 m length, GC-323, GL Science Inc.) was equipped to analyze CO as the reactant and the CO_2 and $C_{1–4}$ light hydrocarbons that were produced. The catalytic performance was also evaluated by CO conversion (%), the selectivity based on carbon for a product (%-C based), space–time–yield (the yield per a weight of

Table 1
Physical properties of the prepared catalysts and ceria supports.

Sample	K_2O or K_2CO_3 (wt.%)	CoO (wt.%)	Group VI metal oxides[a] (wt.%)	S_{BET}[b] (m^2/g)	V_p[c] (cm^3/g)	d_a[d] (nm)	d_{peak}[e] (nm)
Ceria	–	–	–	139	0.19	5.4	3.3
$K_{02}Co_{06}$10MoSi	0.65	3.1	10	177	0.84	19	24
$K_{02}Co_{06}$10MoCe	0.65	3.1	10	71.2	0.14	8	5.4
$K_{005}Co_{06}$11MoCe	0.16	3.1	10	71.6	0.14	8	5.4
$K_{005}Co_{06}$15MoCe	0.25	4.7	15	63.6	0.21	13.1	8.1
$K_{005}Co_{06}$20MoCe	0.33	6.3	20	48.3	0.13	11	9.2
K(C)$_{005}Co_{06}$8.6CrCe	0.39	5.1	8.6	91.1	0.17	7.6	5.4
K(C)$_{005}Co_{06}$15MoCe	0.36	4.7	15	63.9	0.16	9.8	7.1
K(C)$_{005}Co_{06}$22WCe	0.33	4.3	22	58.9	0.15	10	4.8

[a] Group VI metal oxides: MoO_3, WO_3, or Cr_2O_3.
[b] S_{BET}: BET surface area.
[c] V_p: pore volume.
[d] d_a: average pore diameter.
[e] d_{peak}: maximum pore diameter.