

Alcohol Synthesis from Syngas on Group VIII Metal Catalysts Promoted by Mo-Na₂O

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ABSTRACT

The performances of alumina-supported Group VIII metal catalysts promoted by Mo-Na₂O in the synthesis of alcohols from syngas were examined. The activity for alcohol synthesis at 255 °C decreased in the order Rh > Ir > Ru > Pd > Ni > Pt > Cu > Co > Re > Fe. The highest activity for alcohol synthesis was achieved with 3% Rh-5% Mo-1.25% Na₂O/Al₂O₃ (480 g/l cat·h); however, this catalyst showed a rapid decay in activity. Ir-Mo-Na₂O and Ru-Mo-Na₂O catalysts also had a high activity for alcohol synthesis and did not show any decay during the period of the experiments.

INTRODUCTION

Previously, we have found that alumina-supported Ru-Mo-Na₂O [1] and Ir-Mo-Na₂O [2] catalysts have a high activity for the synthesis of alcohols from syngas. The influence of alkaline promoters was examined and it was found that the alkaline component reduces the methanation rate and hence increases the alcohol selectivity [2,3]. The synergistic effect of Ru (Ir) and Mo was also discussed, and it was concluded that alcohols are formed as a result of the close contact between Ru (Ir) and Mo particles [13]. It is interesting, however, that the specific activity for alcohol synthesis of Ru-Mo-Na₂O catalysts seriously depends on the particle size of ruthenium [14]. Therefore, more data about the role of the molybdenum component of the composite catalysts are desirable.

The promoting effects of Mo on Co/SiO₂ [4], Ni/SiO₂ [5] and Rh/SiO₂ [6,7] catalysts were recently discussed by other groups. These papers encouraged us to present here our early work on the comparison of the performances of various metal catalysts promoted by Mo-Na₂O for the synthesis of alcohols from syngas [8].

EXPERIMENTAL

Catalyst preparation

The alumina support (20–35 μm , 130 m^2/g) was prepared by calcination of gibbsite (B303, Nippon Light Metal) at 900°C. The salts used as metal sources were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot 1.5\text{H}_2\text{O}$, $\text{Rh}(\text{NO}_3)_3$, $\text{Pd}(\text{NO}_3)_2$, Re_2O_7 , $\text{IrCl}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. Ammonium heptamolybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$] and sodium nitrate were used as sources of Mo and alkaline components, respectively.

Catalysts were prepared by impregnation of the support with an aqueous solution (1 ml per gram of support) of all the salts necessary for the catalyst components, followed by drying, thermal decomposition at 250°C and hydrogen reduction at 400°C. The nominal concentrations of each metal, Mo and Na_2O were adjusted to be 3, 5 and 1.25 wt.-%, respectively. The detailed procedure for the catalyst preparation is given elsewhere [1,2].

Reaction

The catalyst was tabletted and then pulverized to about 20 mesh. About a 0.4-g portion of the catalyst was placed in a fixed-bed, high-pressure flow reactor made from stainless-steel tubing (I.D. 7 mm). The reactions were carried out under the following conditions: $\text{H}_2/\text{CO}=2$, pressure 9.4 MPa and space velocity (SV) 15 000 h^{-1} . Small portions of the hot effluent gas were repeatedly removed by syringe and analysed by gas chromatography. Six columns were selected to determine the distribution of all the products, viz., MS5A (hydrogen, carbon monoxide, methane), Porapak Q (carbon dioxide), VZ10 (C_1 – C_4 hydrocarbons), porapak N (water, C_1 – C_4 oxygenates, C_1 – C_5 hydrocarbons), sequential PEG 6000 and OV-17 (alcohols up to C_{12} and C_6 – C_{20} hydrocarbons) and DEGS (C_2 – C_{10} hydrocarbons, C_1 – C_4 oxygenated other than alcohols).

When the activity of the catalyst at 255°C was too low to determine the precise product distribution, the reaction temperature was progressively raised to 300°C and then to 350°C. The reactions were maintained for 6 h on-stream at a particular temperature. Effluent gas, reduced to atmospheric pressure, was led to a condenser immersed in a dry-ice bath and liquid products were collected over the period of 6 h. The alcohol synthesis activity (STY_{alc}) of the catalyst was determined on the basis of the weight and the analysis (Porapak N, DEGS and PEG 6000–OV-17 columns) of this liquid product and was, therefore, the average value for the 6-h reaction period. The values of SV and STY are based on the catalyst volume calculated from the bulk density of the tabletted catalyst.

RESULTS AND DISCUSSION

The performances of the alumina-supported metal-Mo-Na₂O catalysts are presented in Table 1. The results can be summarized as follows.

All the catalysts afforded a series of straight-chain primary alcohols. The alcohol synthesis activity of the catalysts depended on the main catalyst component and decreased in the order Rh > Ir > Ru > Pd > Ni > Pt > Cu > Co > Re > Fe. This order roughly resembles the ranking for methanation activity of unsupported metal catalysts reported by Fischer et al. [9]. The Pd catalyst showed a much higher activity than predicted by Fischer et al.'s ranking; however, the high methanol synthesis activity of an unpromoted Pd catalyst has been reported [10].

The highest activity (480 g alcohol/l cat·h) and selectivity (69%, excluding carbon dioxide) for alcohol synthesis was achieved with 3%Rh-5%Mo-1.25%Na₂O/Al₂O₃. However, this catalyst exhibited a rapid decrease in activity: its initial alcohol synthesis activity was more than double that of the Ir-Mo-Na₂O catalysts, whereas at the end of the experiments (6 h) the activity was one quarter of the initial activity. The other catalysts showed stable activities during the same reaction period.

The condensates from all the catalysts were homogeneous, clear solutions containing 20-90% alcohols. The absence of higher hydrocarbons in the condensates is an important feature of the present catalyst system. The molybdenum component seems to have an inhibiting effect on the propagation of

TABLE 1

Performance of the metal-Mo-Na₂O catalysts for alcohol synthesis from syngas

Reaction conditions: H₂/CO=2, pressure 8.4 MPa, SV = 15 000 h⁻¹.

Metal	Reaction temperature (°C)	CO conversion (%)	STY _{cond} (g/l·h)	Alcohol in condensate (%)	STY _{alc} (g/l·h)	C atom selectivity (%)		
						Alcohols	CH ₄	Other hydrocarbons
Fe	350	15	-	-	27 ^a	9.0	46	45
Co	300	9.6	390	19	75	30	56	14
Ni	300	18	290	56	160	36	36	28
Cu	300	17	200	61	120	31	33	36
Ru	255	23	480	56	270	46	30	24
Rh	255	22	530	91	480	69	18	12
Pd	255	4.6	76	51	39	54	30	16
Re	300	6.0	-	-	7.7 ^a	5.7	62	32
Ir	255	21	420	83	350	57	28	15
Pt	300	10	180	67	120	28	55	17

^aBecause of the low activity of the catalyst, STY_{alc} was determined from gas-phase analysis.

carbon chains. All the catalysts exhibited a high selectivity for the formation of carbon dioxide, suggesting that molybdenum components also facilitate the water gas shift reaction. This seems to be another reason for the homogeneity of the condensates because of the low yield of water.

Anderson-Schulz-Flory (A-S-F)-type plots for the carbon number distributions of the alcohol products formed on metal-Mo-Na₂O/Al₂O₃ are presented in Figs. 1 and 2. All the plots exhibited curvature; this deviation from simple A-S-F kinetics may be explained by one of the following reasons. One is the heterogeneity of the practical surface; as two extreme cases, a two-site model and a distributed site model have been proposed [11,12]. Both models will give concave curves in A-S-F-type plots and the values obtained by the two-site model analysis are given in the captions of Figs. 1 and 2. Another reason is violation of Anderson's assumption [15]. Because of steric and/or inductive effects, the ratio of the rate of termination (formation of an alcohol of carbon number n from an intermediate) to the rate of propagation (formation of another intermediate which will give an alcohol of carbon number $n + 1$), $(k_t/k_p)_n$, can depend on the carbon number, n (Herrington's assumption, ref. 16). If $(k_t/k_p)_n$ decreases (increases) with increasing n , then theoretical carbon number distribution will give a concave (convex) curve in an A-S-F-type

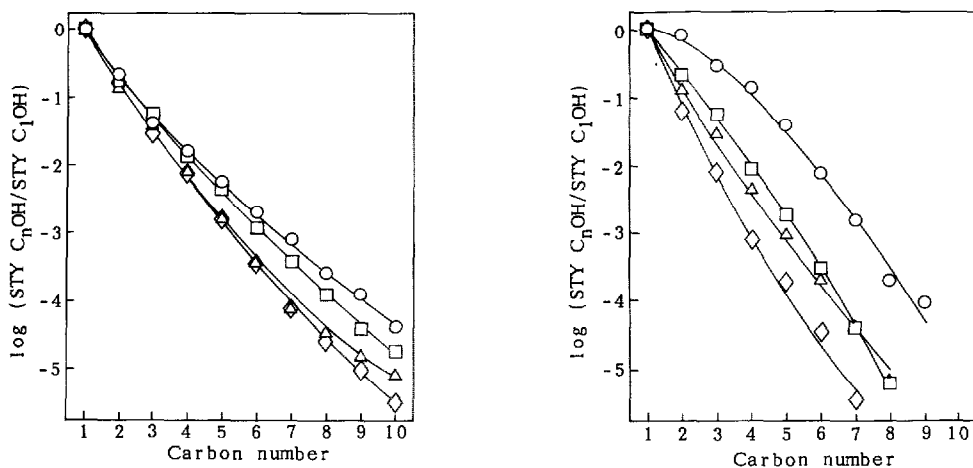


Fig. 1. Carbon number distribution of alcohols formed on alumina-supported Ru (\circ), Pd (Δ) and Ir (\diamond) catalysts promoted by Mo-Na₂O. Reaction conditions: 255°C, H₂/CO=2, pressure 8.4 MPa, SV=15 000 h⁻¹. α values determined by the two-site model: Ru, $\alpha_1=0.04$, $\alpha_2=0.37$; Pd, $\alpha_1=0.15$, $\alpha_2=0.31$; Rh, $\alpha_1=0.19$, $\alpha_2=0.48$; Ir, $\alpha_1=0.18$, $\alpha_2=0.36$.

Fig. 2. Carbon number distribution of alcohols formed on alumina-supported Co (\circ), Cu (Δ), Ni (\square) and Pt (\diamond) catalysts promoted by Mo-Na₂O. Reaction conditions: 300°C, H₂/CO=2, pressure 8.4 MPa, SV=15 000 h⁻¹. α values determined by the two-site model: Cu, $\alpha_1=0.12$, $\alpha_2=0.20$; Pt, $\alpha_1=0.06$, $\alpha_2=0.17$.

plot. The abnormal convex plots for Co–Mo–Na₂O and Ni–Mo–Na₂O may be explained by an increase in $(k_t/k_p)_n$ with increasing n . The chain growth probability had a tendency to decrease with increase in the atomic number of the catalyst when compared within the same period of the Periodic Table, although those of Rh and Pd catalysts showed an opposite tendency: Co > Ni > Cu, Ru > Pd > Rh, Re > Ir > Pt. The Ru–Mo–Na₂O/Al₂O₃ catalyst seemed to be the most suitable for the formation of higher alcohols.

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