

Communication

Synthesis of C₂ oxygenated compounds from syngas in supercritical cyclohexane

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Catalytic synthesis of C₂ oxygenated compounds from syngas in supercritical cyclohexane was reported in this paper. The effect of the molar ratio of media to feed on the conversion and selectivity was mainly discussed. The results showed that the selectivity of C₂ oxygenated compounds in supercritical cyclohexane was greatly improved, and the by-products of acetic acid, acetic ester and alkanes were efficiently suppressed. Although the CO conversion was slightly declined, the space-time yield of C₂ oxygenated compounds basically kept the constant at high media/feed ratio.

Keywords Supercritical cyclohexane, Rh-catalyst, C₂ oxygenated compounds

C₂ oxygenated compounds including ethanol and acetaldehyde are one kind of important chemicals. The catalytic conversion of syngas into C₂ oxygenated compounds over Rh-based catalysts has been attracting much attention.¹⁻³ But the by-products of acetic acid, acetic ester and alkanes were largely produced in gas phase, and badly restricted the selectivity of main products and the economy of this process. At present most of investigators only paid attention to the exploration and modification of the catalyst. The selectivity of the main products is hardly enhanced although the catalysts have been highly improved. Therefore, new technique is required to improve the process.

The heterogeneous catalytic reaction in supercritical phase has attracted a great deal of interest in recent years and the research in this area has led to a number of practical applications which were reviewed elsewhere.^{4,5}

The advantages of supercritical process over conventional gas-phase process included the improvement of desirable product selectivity, higher reaction conversion and reaction rates, and the maintenance of the activity because of the enhancements of the physicochemical properties of the fluid in the critical state⁶⁻⁸ (*i. e.*, liquid-like density, gas-like diffusion and high compressibility). Thus, the catalytic synthesis of syngas to C₂ oxygenated compounds was conducted for the improvement of the reaction performance in supercritical phase. Here, the cyclohexane was chosen as supercritical media (reaction conditions: $T = 593$ K, $GHSV = 3000$ h⁻¹, $P_G = 3.0$ MPa, $P_{SC} = 6.0$ MPa).

The syngas composition was given in Table 1. The supercritical catalytic synthesis of syngas to C₂ oxygenated compounds was carried out over commercial Rh/SiO₂ catalyst supplied by Dalian Institute of Chemical Physics at the supercritical cyclohexane in a downflow fixed bed reactor with inner diameter of 1.2 cm. The products were determined by gas chromatography. Gas phase products CO, H₂, CO₂ and CH₄ were separated on a 2m carbon molecule sieve and detected by TCD (pressure 200 kPa, column temperature 100°C, flow speed 60 mL/min, current 70 mA) while the hydrocarbons were separated on a 2m Porapak Q and detected by FID (pressure 200 kPa, column temperature 120°C, flow speed 60 mL/min). Liquid products such as alcohol, aldehyde were analyzed on a 2m Chromosorb 101 by FID and acetic acid was determined by NaOH solution titration.

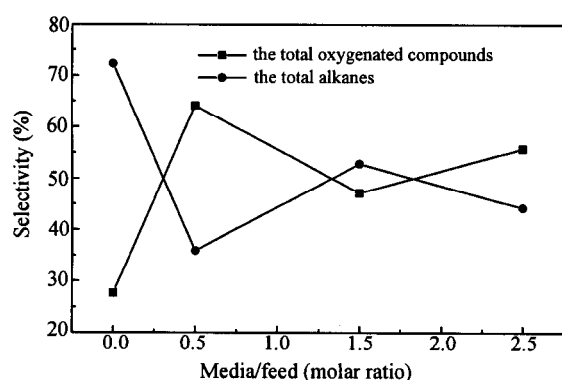
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Table 1 The composition of syngas

Component	CO	H ₂	CH ₄	CO ₂
Composition, Vol. %	64.10	34.30	0.25	1.30

The properties of the system in supercritical phase are very sensitive to pressure.⁹ Because the change of pressures is identical to the molar ratio of supercritical medium to feed in this reaction, the molar ratio of medium to feed was selected as the main operation variable to adjust supercritical phase behavior. The typical results were showed in Fig. 1 and Table 2.

**Fig. 1** The effect of the molar ratio of media to feed on the selectivity of total oxygenated compounds and total alkanes.**Table 2** Effect of media/feed (molar ratio) on CO conversion and space hour yield (SHY) of oxygenated compounds and alkanes

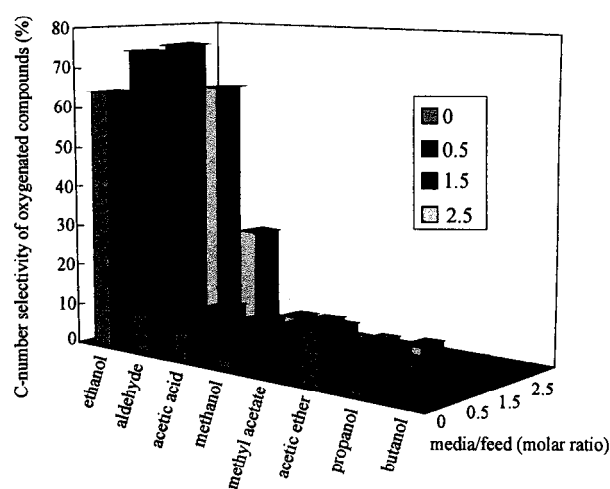
Media/feed (molar ratio)	0 ^a	0.5	1.5	2.5
Conversion (%)	30.73	10.75	13.79	14.14
SHY of total oxygenates (mg/(g(cat.)·h))	183.44	151.68	144.69	171.55
SHY of total alkanes (mg/(g(cat.)·h))	334.10	58.15	109.50	94.23

^aThe reaction was carried out in gas phase without supercritical solvent.

Fig. 1 shows that the selectivity of oxygenated compounds in supercritical cyclohexane was much higher than that in gas phase, but the selectivity of the alkanes greatly decreased in supercritical phase. The main reason could be due to the easy desorption of alkanes over the catalyst surface in supercritical cyclohexane,¹⁰ which led to a great decrease in SHY of total alkanes (see Table 2). Furthermore, CO conversion also declined in supercritical phase, which might be contributed to either

the capillary condensation of supercritical fluids taking place in catalyst pore so that the diffusion of feedstock was restrained¹⁰ or the dilute effect of supercritical fluid as inertia medium. However, it was very important that the space-time yield of oxygenated compounds basically maintained the constant at higher media/feed. These indicated that oxygenated compounds were more favorable than alkanes in supercritical cyclohexane.

Table 3 shows the C-number distribution of oxygenated compounds and alkanes in different phase (Fig. 2 and Fig. 3). In supercritical phase, the selectivity of C₂ oxygenated compounds, including ethanol and acetaldehyde, was greatly enhanced, and the selectivity of ethanol reached maximum at media/feed = 1.5, and the product of acetaldehyde seemed comparative with that of ethanol as the molar ratio of media to feed increased, which might be due to the change of supercritical behavior with media/feed. In any cases, the selectivity of acetic acid, acetic ester and C₃, C₄ alcohol decreased. This indicated that the interaction between supercritical cyclohexane and C₂ oxygenated compounds was stronger than that of supercritical cyclohexane with higher carbon alcohol and acetic acid, which could be due to the change of the reaction activated volume in supercritical phase.¹¹ For C-number distribution of alkanes, the selectivity of methane was improved because of long chain alkanes were effectively restrained.

**Fig. 2** C-number distribution of oxygenated compounds in different phases.

From above results, it could be concluded that introduction of supercritical cyclohexane into the reaction

system was effective to improve the selectivity of C₂ oxygenated compounds and to suppress the by-products of acetic acid, acetic ester and alkanes. Although in supercritical cyclohexane CO conversion slightly decreased, the space-time yield of oxygenated compounds was similar to that in gas phase. Thus, a new route was provided for catalytic synthesis to C₂ oxygenated compounds from syngas.

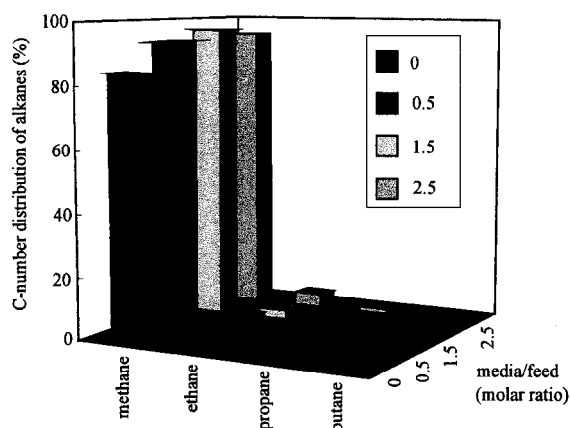


Fig. 3 C-number distribution of oxygenated compounds in different phases.

Table 3 C-number distribution of oxygenated compounds and alkanes in different phase

Media/feed (molar ratio)	C-number distribution of oxygenated compounds (%)			
	0	0.5	1.5	2.5
ethanol	64.23	73.75	75.01	63.23
aldehyde	9.25	6.78	6.89	25.16
acetic acid	7.00	5.92	5.60	3.97
methanol	2.67	4.73	6.29	3.23
methyl acetate	0.89	2.08	1.62	1.52
acetic ether	15.05	6.19	3.58	2.28
propanol	0.91	0.54	0.99	0.60
butanol	0.00	0.00	0.00	0.00
total alkane				
methane	84.10	93.33	96.52	94.65
ethane	7.65	5.55	3.02	4.01
propane	6.11	1.07	0.42	1.17
butane	2.13	0.04	0.03	0.16

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