Olefine Production from Syngas over Bimetallic Supported

Sh.S. Itkulova* and G.D. Zakumbaeva

D.V.Sokolsky Institute of Organic Catalysis and Electrochemistry,

142 Kunaev St., 480100 Almaty, Kazakhstan

Abstract

Bimetallic cobalt-containing catalysts supported on alumina have been studied in the Fischer-Tropsch synthesis. It has been shown that a promotion of Co/Al_2O_3 by iridium leads to dispergation of both metals. It was supposed that the metal dispergation occurred due to M-M interaction with formation of the bimetallic nano-particles of cluster type. These particles have the high catalytic activity, selectivity and stability in the Fischer-Tropsch synthesis. It was observed that by regulation of the process conditions it is possible to obtain the definite hydrocarbon fractions. Thus, the increase both $CO+H_2$ ratio and space velocity is accompanied by high olefin yield.

Introduction

Syngas ($CO+H_2$) is recognised as an alternative and perspective raw material for production of the synthetic oil fractions. Syngas may be produced by a conversion of different carbon-containing sources such as light paraffins included into the composition of natural, casing- head gases and gases of petrochemical processing, biomass, wastes, coal and others, as well as by a new method of CO_2 reforming of methane [1,2]. At present, the production of methanol and different hydrocarbons from syngas obtained by conversion of natural gas or coal have been used in industry [1].

The possibility to obtain the different useful products, for example, olefins gives impulse to the development of process on the base of syngas (Fisher-Tropsch Synthesis). Because of oil composition is characterised by low content or absence of olefins and usual methods of olefin production by benzene pyrolysis and catalytic cracking have the high power capacity the development of effective methods of olefin production is an actual problem. Method of production of olefins from methanol obtained from syngas has been worked out by «Mobil oil» (USA) [3]. It was expected that the industrial implementation of this project decreases the power capacity [4, 5].

Because of $CO+ H_2$ process is the catalytic one its

efficiency may be increased by design and use of new selective catalysts, which are able to regulate the composition of formed products and to decrease the power capacity of the process.

This paper deals with the study of cobalt-containing modified and supported on alumina catalysts and conditions for direct obtaining of olefins from syngas. It is known that addition of the second metal to the catalyst composition and loading active phase to the support can lead to new unpredictable phenomena because of M-M and/or M-support interactions.

Experimental

a) Catalyst preparation

Bimetallic Co-containing catalysts were prepared by impregnation of the Al_2O_3 support with a solution containing both the Co and the Ir compounds and following thermal treatment. The total metal concentration in the catalyst was 10 wt%. Iridium content in bimetallic catalysts was varied from 0.5 to 50 wt% from total metal content. Below Ir amount has been indicated as percentage by mass from all metal content (Co + Ir).

b) Catalyst characterisation

The phase composition, microstructure, local chemical composition, electronic states of the metals and their distribution over the surface, adsorptive proper-

*corresponding author. E-mail: adm@orgcat.academ.alma-ata.su

ties of catalysts at different stages of preparation and operation were studied by using: X-Ray analysis (difractometer with CuK_α and CoK_α radiation), transmission electron microscopy at a resolution of about 0.5 nm, IR-spectroscopy and XPS.

Specimens for TEM-analysis were prepared with conventional methods including dried suspension and «replica».

Infrared spectra were measured after the CO adsorption (T=298K) and after CO+ H_2 reaction (P=0.1 MPa, T=473K, experiment time 30-120 minutes) over Co-Ir/ Al_2O_3 catalysts

with using conventional KBr-cell combined with a flow reactor at room temperature in the wavenumber range of 1400 to 2400 cm^{-1}.

For XPS-analysis the residual pressure inside the spectrometer was 10^{-4} Pa. The binding energies of standard compounds were referenced to C1s line at 285.0 eV. Binding energy values were measured with 0.1 eV precision.

The specific surface area were measured by the BET method from the adsorption of nitrogen at liquid nitrogen temperature.

The degree of reduction of cobalt ions to cobalt metal was obtained from hydrogen consumption which was measured in a closed system with a gas circulating unit. The degree of cobalt ion reduction has been calculated as a ratio of number of cobalt atoms in zero-valency state to total calculated number of cobalt atoms in catalyst.

c) Catalyst testing

The hydrogenation of CO was carried out in a flow reactor. The CO+ H_2 mixtures with different CO/ H_2 ratio (1/4-3/2) were prepared. 10% nitrogen was added to reaction mixture as a inner standard. The reaction was studied at variation of pressure from 0.1 to 2.0 MPa, temperature from 423 to 553K and space velocity from 100 to 2000 hr^{-1}, experiment time was 3-100 hours.

The stability of Co-Ir/ Al_2O_3 was tested in pilot conditions with the commercial synthesis gas produced by conversion of natural gas. The composition of the commercial synthesis gas is given in Table 1. The duration of continuous exploitation was more than 2000 hours.

d) Analysis of reaction products

The reaction products were analysed by gas chromatography and fractional distillation. Viscosity, density, average molecular mass, boiling and solidifica-

Table 1
The composition of commercial synthesis gas (vol. %)

carbon oxide	25-30%	carbon dioxide	7-10%
hydrogen	65-70%	nitrogen	1-3%
methane	1-4%	S-containing compounds	up to 0.2mg/m^2

tion points, refraction index of the liquid hydrocarbons were determined by standard methods. After the separation of super-hard hydrocarbons their drop point was established.

Results and discussion

a) Iridium influence on composition and structure of Co/ Al_2O_3

10% Co-Ir/ Al_2O_3 catalysts has been studied by X-ray analysis. No diffraction patterns have been obtained for all of the catalyst samples. These results indicate that metals present in catalysts in X-ray amorphous and high dispersed phases.

To determine the morphology, microstructure and local chemical composition of bimetallic catalysts the investigation by transmission electron microscopy has been carried out. Small spherical particles in the 10%Co-Ir/ Al_2O_3 with small content Ir (0.5-5 wt%) were found by a specific brightness in dark-field of shot (Fig.1). The particles are uniformly distributed on the support surface. No microdiffraction patterns have been obtained. The particle size is less than 2.0 nm. It should be taken into account that the measurements were carried out on the basis of dark-field microphotographs. This is a reason that the measured particle sizes are significantly higher than the real ones.

The main elements of the structure of catalysts with high Ir loading (50 wt%) are spherical particles with size < 2.0 nm. At the same time the «needle» shape particles with the length of 2.0-5.0 nm were observed at a bright-field survey. Microdiffraction analysis of latter structures showed that they were attributed to Ir.

It is necessary to note that Co-particles in monometallic 10% Co/ Al_2O_3 have the spherical shape and more than 85% of particle have size of 3.0-7.0 nm (Fig.2).

Ir-particles in 10% Ir/ Al_2O_3 mostly have «needle» shape with up to 60.0 nm length and 10.0 nm width, which are combined in pairs and negligible part of Ir is presented in spherical form with various sizes of

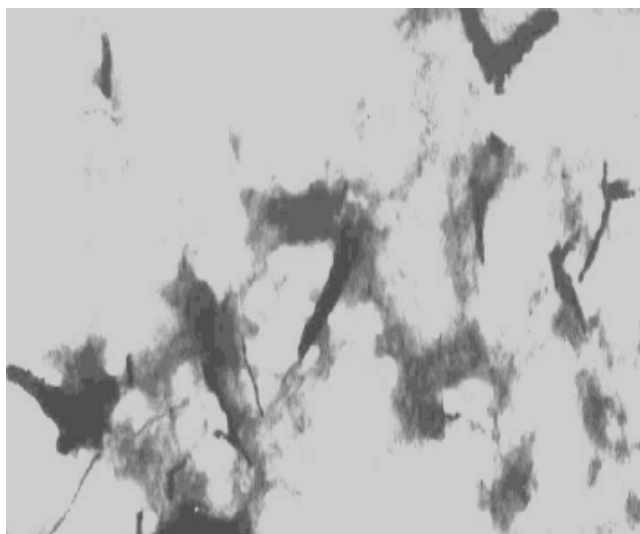Fig.1.TEM pattern of 10% Co-Ir (95:5)/Al₂O₃ catalyst (dark-field) (magnification is 200,000)

Fig.2.TEM pattern of 10 % Ir/Al₂O₃ catalyst (magnification is 500,000)

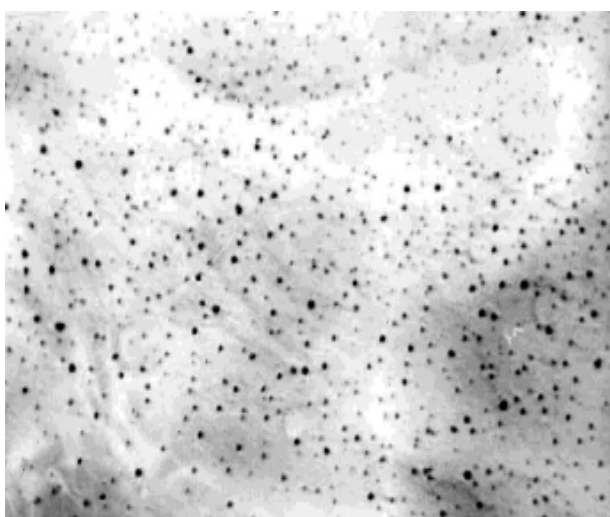Fig.3.TEM pattern of 10% Co/Al₂O₃ catalyst (1 cm corresponds to 140 nm)

particles (from 1.0 to 60.0 nm) (Fig.3).

The obtained results show that Ir addition to the Co/Al₂O₃ catalyst composition leads to the dispergation of both metals. Absence of microdiffraction patterns and small particle sizes (<<2.0 nm) give possibility to suppose the formation nano-structures of a cluster type. The reducing of particle size with the increase of Ir loading from 0.5 to 50 wt% indicates the strengthening of Co-Ir interaction result in the formation of bimetallic clusters.

The formation of heterometallic clusters has been approved by electron microscopy study used «replica» method, when catalyst sample was treated by hydrof-luoric acid. Phases of unnoble metals such as Co and Al have to be removed at the use of this method. The study of treated 10% Co-Ir(95:5)/Al₂O₃ shows the formation of only spherical particles. No microdiffraction picture of these particles has been observed. At the same time they are characterised by brightness in dark-field. These structures can be attached only to bimetallic Co-Ir clusters. Because of the amount of spherical particles is high and the concentration of Ir in this catalyst is low (5 wt%) it is impossible to attach all spherical particles to Ir.

In catalyst with high content of Ir (50 wt %) the appearance of «pure» Ir phase besides bimetallic clusters has been observed. It is clear that in this case the loading of Ir is an excess. The atomic ratio Co-Ir (50:50)/Al₂O₃ is about 3. It is possible to suppose that bimetallic clusters are enriched with cobalt atoms and have «cherry» shape structure as it has been proposed for Ru-Cu-catalyst [6]. Ir atom is surrounded by Co atoms.

At high Co-content (95-95.5 wt%) it is possible to suppose formation of small amount of monometallic Co-clusters. Consequently the real atomic Co/Ir ratio may be less than calculated one.

It has been shown that particle dispergation increases after catalyst reduction by hydrogen and treatment by CO + H₂ reactant mixture.

The high thermostability of bimetallic clusters has been observed. The agglomeration of clusters controlled by TEM is started at T is about 1073 K. Only high dispersed X-ray amorphous phase has been found in catalyst tested in industrial conditions during more

than 2000 hours.

It has been found by XPS that the reduction of 10% Co-Ir/Al$_2$O$_3$ leads to enriching of catalyst surface with Co and Ir atoms. Change of the Ir$_s$/Ir$_v$ ratio is more significant (Ir$_s$ is surface atoms, Ir$_v$ is total calculated amount Ir atoms). Ir$_s$/Ir$_v$ ratio increased from 0.96 to 16.25 with the decrease of Ir loading from 50 till 0.5 wt% in the bimetallic catalysts. These results indicate that practically all Ir atoms in catalyst with small its content are located on the surface and stabilised by Co. Co$_s$/Ir$_s$ in all samples is much higher than 1. Binding energies Co 2p$_{3/2}$ and Ir 4f$_{7/2}$ in reduced 10% Co-Ir/Al$_2$O$_3$ (Ir is 0.5-50 wt%) are significantly higher than these values for massive crystal Co^o and Ir^o. It can be explained by the high metal dispersity and interaction of metals with support [7,8].

It is necessary to note that Co remains in zero-valency state after catalyst exposing in air. The degree of Co reduction in freshly reduced Co-Ir(95:5)/Al$_2$O$_3$ is 64.5% and after exposing in air during 1 hour the reduction degree is 62.3%.

Reproducibility of Co increases with the increase of Ir loading. The degree of Co reduction in samples with 2 and 5 wt% Ir loading is 59.0 and 65.7% respectively. At the same time the degree of Co reduction in 10% Co/Al$_2$O$_3$ is 40.1%. The optimum degree of Co reduction for Fischer-Tropsch Synthesis is varied in the range of 56-66%. Catalyst with low degree of Co reduction is less active in CO + H$_2$ reaction. On the other hand the reaction methanisation prevalences on the catalyst with high degree of Co reduction.

The appearance of two intensive bands at 2115 and 2170 cm^{-1} in the carbonyl region was observed at CO adsorption on 10% Co-Ir/Al$_2$O$_3$ (Ir < 50 wt%) by IR-spectroscopy. These carbonyls are characterised by a weak M-CO binding and are removed after treatment of catalyst by inert gas during 5 minutes. These bands can be attached to linear chemisorbed CO on high dispersed Co-centres.

CO adsorption on monometallic Ir is characterised by bands at < 2100 cm^{-1} and these Ir carbonyls are stronger binded.

Additional band at 2050 cm^{-1} is appeared in catalyst with high Ir content (50 wt%). This band was attached to strong binded linear Ir carbonyls. At the beginning of CO + H$_2$ reaction over 10% Co-Ir/Al$_2$O$_3$ the bands at 2115 and 2170 cm^{-1} are observed in the IR-spectra and then these bands disappeared. It indicates that carbonyls actively take part in the further conversions.

These results confirm the strong Ir influence on the composition, structure and adsorption properties of Co-containing catalysts. Even small addition of Ir leads to formation of bimetallic nano-structures of cluster type. These clusters are characterised by high thermostability.

b) Conditions for olefin production from syngas over 10% Co-Ir/ Al$_2$O$_3$

Earlier it has been reported by us [9-13] that the main products of CO+ H$_2$ reaction over Co-containing supported on Al$_2$O$_3$ catalysts are the hydrocarbons.

In present study it was shown that the process parameters such as a ratio of CO/ H$_2$, space velocity and temperature are substantial factors influenced on olefin yield.

The increase of experiment temperature leads to increase both CO conversion and hydrogenation properties. At the highest temperatures methane is only one reaction hydrocarbon product. The increase temperature from 423 up to 473K over 10% Co-Ir(95:5)/ Al$_2$O$_3$ is accompanied by increase of CO conversion from 48.1 up to 100%. The methane yield is 10.0-10.9% at T$_{exp}$ = 423-443K. Further temperature increase up to 473K leads to raising of methane yield up to 52.3% (CO/ H$_2$ =1/2.2, P=0.1 MPa, space velocity = 100 hr^{-1}). The olefin/paraffin ratio is 0.17-0.19 at the T$_{exp}$=423-443K. With further raising of T$_{exp}$ up to 473K olefins completely disappear from reaction products (Table 2).

It has been found that decrease of H$_2$ content in reaction mixture promotes the process of olefins (C$_2$-C$_{25}$) formation. For instance, ethylene is appeared in the products composition at CO/ H$_2$ =1/1. At lower CO/ H$_2$ ratios ethylene is not detected (P=1.0 MPa, space velocity = 1000 hr^{-1}) (Table 3). The ethylene content in ethylene/ethane fraction increases from 4 to 20% with the increase of CO/ H$_2$ ratio from 1/1 up to 3/2 (Table 3). Content of propylene in propylene/propane fraction, butylene in butylene/butane fraction and olefins in C$_{5+}$ fraction increase from 8.0 up to 76.0, from 5.0 up to 68.0 and from 5.0 up to 59.0% respectively with increase of CO/ H$_2$ ratio from 1/4 up to 3/2 (Table 3).

Space velocity strongly influences on the olefin yield. With increase of this parameter, i.e. with decrease of contact time, the prevailing yield of olefins is observed. Thus, the increase of space velocity from 100 up to 1500 hr^{-1} leads to the increase of propylene content in propylene/propane fraction from 10.0 to 57.0% (CO/ H$_2$ =1/2.2, P=1.0 MPa) (Table 4). The

Table 2

Influence of experiment temperature on the yield and composition of CO hydrogenation products over
Co-Ir(95:5)/ Al_2O_3 (CO/ H_2 =1/2.2, P=0.1MPa, space velocity-100 hr^{-1})

T_{exp}, K	CO conversion, %	Yield, %			Ratio of olefin / paraffin
		C_1	C_{2+}	CO_2	
423	48.1	10.9	87.5	1.6	0.17
443	61.1	10.0	88.3	1.7	0.19
453	75.7	18.4	72.9	8.7	0.09
473	100	52.3	17.7	30.0	-

Table 3

Influence of CO/ H_2 ratio on olefins yield at CO hydrogenation over
10% Co-Ir(95:5)/ Al_2O_3 (1.0 MPa, space velocity=1000 hr^{-1})

T_{exp}, K	CO conversion, %	Yield, %			Ratio of olefin / paraffin
		C_1	C_{2+}	CO_2	
423	48.1	10.9	87.5	1.6	0.17
443	61.1	10.0	88.3	1.7	0.19
453	75.7	18.4	72.9	8.7	0.09
473	100	52.3	17.7	30.0	-

* In the table shows the T_{exp} are optimum for given ratio CO/ H_2

Table 4

Influence of space velocity on the olefin yield at CO hydrogenation over
10% Co-Ir(95:5) /Al_2O_3 (P=1.0 MPa)

CO/ H_2	Space velocity hr^{-1}	T_{exp},K *	Conversion of CO, %	Total yield of C_{2+}	Content of olefins in fractions %			
					C_2	C_3	C_4	C_{5+}
1/ 2.2	100	453	75.7	87.5	traces	10.0	17.0	8.0
	400	493	84.4	93.3	-	21.0	14.0	10.0
	1000	498	87.1	93.8	-	30.0	12.0	10.0
	1500	508	90.0	93.8	-	57.0	31.0	24.0
2/ 3	1000	523	86.3	86.1	-	56.0	25.0	20.0
	1500	523	80.0	88.0	traces	59.0	27.0	25.0
	2000	528	78.3	90.1	4.0	63.0	32.0	30.0

increase of space velocity from 1000 to 2000 hr^{-1} at CO/H_2 =2/3 causes the increase of propylene content from 56.0 to 63.0 and olefins of C_{5+} fraction from 20.0 to 30.0% in respective fractions (Table 4).

Thus to prevalence of olefin formation it is desirable to carry out the process at higher CO/H_2 ratios and space velocities. It is needs to take into account the necessity of the increase of experiment tempera-

ture for running of the process at higher CO/H_2 ratios and space velocities. It leads to decrease of formation of higher molecular hydrocarbons.

The decrease of H_2 content in the reaction mixture result in the increase of CO_2 formation. This is a reason of decrease C_{2+} hydrocarbon yield from 95.9 to 67.6% at the increase of CO/H_2 ratio from 1/4 to 3/2 (Table 3). That is why the choice of reaction conditions in each case depend on a type of required hydrocarbons fractions.

Conclusion

Addition of Ir to Co/Al_2O_3 catalyst composition promotes metal dispergation due to Co-Ir interaction. The interaction between Co and Ir leads to the formation of bimetallic nano-particles of cluster type.

These nano bimetallic clusters have the high activity, selectivity and stability in Fischer-Tropsch synthesis.

It is possible to obtain ordered hydrocarbon fraction by variation of the process conditions, in particular the formation of olefins may be increased at use of high space velocity and CO/H_2 ratio.

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