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Review

Progress in synthesis of ethylene glycol through C₁ chemical industry routes

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ABSTRACT

Ethylene glycol (EG) is an important industrial chemicals. It has attracted attention because it can be used to synthesize polyester resins and fibers. C₁ chemical industry routes have been explored for EG synthesis from syngas and coal as starting materials. It is suggested that such routes are more promising methods for EG synthesis than the use of petroleum is. The pertinent literature on EG synthesis through C₁ chemical industry routes are summarized. The methods include direct synthesis from syngas, carbonylation of formaldehyde, CO coupling reactions, hydroformylation of formaldehyde, and condensation of formaldehyde.

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1. Introduction

The imbalance between supply and demand for energy resources worldwide has led to the development of petroleum substitutes. One of the important measures for solving this problem is the synthesis of organic chemical raw materials from natural gas and coal through C₁ synthesizing processes, e.g., using syngas. Although coal accounts for 96% of the primary energy structure in China, which is the largest coal producer in the world, more than 75% of the coal is used as low-efficiency fuel. C₁ chemistry has therefore become important in China in terms of reducing the serious pollution caused by the coal industry and developing clean organic materials technologies. Ethylene glycol is an important organic chemical raw material, and is used in the production of polyester fibers, antifreeze, unsaturated polyester resins, plasticizers,

and surface active agents. Ethylene glycol has also been extensively used in the tobacco, textile, and cosmetics industries. China has the world's largest ethylene glycol consumption, 90% of which is used in the production of polyester. In recent years, the rapid development of China's polyester industry has greatly increased the demand for ethylene glycol. However, the limited production capacity of ethylene glycol in China has led to annual increases in imports of ethylene glycol. This in turn has caused the imbalance between supply and demand for ethylene glycol to increase significantly [1]. It has been reported that the consumption of ethylene glycol in China in 2010 was 9.139 million tons, and is expected to reach 11 million tons in 2014, an average growth rate of 7.2% per year.

At present, ethylene glycol is mainly produced from ethylene via hydration of ethylene oxide. The disadvantages of this method include the high moisture content of the product, a

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Scheme 1. Main processes for ethylene glycol production.

complicated purification process, high energy consumption, and low yield. Since the 1970s, because of the scarcity of oil, efforts have been made to replace oil by abundant and cheap natural gas or coal in the preparation of ethylene glycol, and great progress has been achieved. Ethylene glycol can be synthesized from syngas as the starting material, using either a direct process or an indirect process; the process routes are shown in Scheme 1. In the direct process, ethylene glycol is synthesized from syngas directly. In the indirect process, ethylene glycol is synthesized from syngas via methanol, formaldehyde, or other intermediate compounds, e.g., by carbonylation of formaldehyde, CO coupling reactions (oxalation), hydroformylation of formaldehyde, and condensation of formaldehyde.

2. Direct synthetic process

The direct synthesis of ethylene glycol from syngas is an “atom economic reaction”, which exhibits high use of raw materials. Chen et al. [2] studied the thermodynamics of this reaction and concluded that the reaction is thermodynamically favorable when the reaction temperature is lower than 81.5 °C, but highly active catalysts are necessary to improve the low reaction rate. High pressure was conducive to shifting the equilibrium towards the direction of the products, but this would increase the production costs.

In 1948, DuPont [3] first reported the synthesis of ethylene glycol directly from syngas, using $\text{Co}_2(\text{CO})_8$ as a catalyst, under a pressure of 304 MPa. However, the harsh reaction conditions and low yield of ethylene glycol could not satisfy the requirements of large-scale industrial production. In the 1970s, UCC [4,5] reported the direct synthesis of ethylene glycol from syngas, using a rhodium–carbonyl complex as the catalyst, in an organic solvent such as tetrahydrofuran, methanol, or isopropanol. However, there were problems such as the unstable nature and low catalytic activity of the catalyst, high pressure, and low selectivity. UCC [6] later developed bulky alkylphosphine and amine-modified rhodium–carbonyl complexes with significantly improved catalytic capacities and selectivities using dimethoxytetraglycol as the solvent. By using this type of catalyst, the reaction temperature and pressure could be reduced to 230 °C and 49.0 MPa, respectively. Under

the conditions of $n(\text{H}_2)/n(\text{CO}) = 1$, the selectivity and space time yield of ethylene glycol were 67% and 259 g/(L·h), respectively, with propylene glycol, glycerin, and methanol as by-products. Although promising improvements were achieved, the total conversion of syngas and the product selectivity were still relatively low.

In 1987, Murata et al. [7] developed new imidazolium-modified Ru catalysts, which have good catalytic capacities as a result of the strong coordination and basicity of imidazolium. In the presence of $\text{Ru}_3(\text{CO})_{12}$, 1-methyl-3-ethyl-benzimidazolium bromide, and Et_3N , an ethylene glycol yield of 41.3% was obtained under conditions of 150 °C/10 MPa. Mitsui Chemicals and Sumitomo Chemical [8] obtained high catalytic activities and selectivities (70%) in the synthesis of ethylene glycol using Ru 1-alkyl-2-substituted benzimidazolium compounds as catalysts and dimethoxytetraglycol as the solvent. They also found that the catalytic activity improved significantly with increasing concentration of imidazolium and its derivatives. Unfortunately, some *N*-methylbenzimidazolium decomposed under these reaction conditions.

Masuda et al. [9] studied the reaction mechanism of the direct synthesis of ethylene glycol from syngas. They found that the selectivity for ethylene glycol improved with increasing partial pressure of hydrogen, and the amount of methanol by-product decreased. The selectivity for another by-product, methyl formate, changed little with variations in the partial pressure of hydrogen. The partial pressure of CO hardly affected the selectivity for ethylene glycol. The proposed mechanism (Scheme 2) suggested that formaldehyde was the reaction intermediate, and its formation and configuration would determine the catalytic activity and product selectivity.

At present, the direct synthesis of ethylene glycol from syngas is still under investigation. There is still a long way to go to achieve large-scale industrial production of ethylene glycol because of current problems such as harsh reaction conditions, decomposition of the catalysts under the current reaction conditions, a complicated separation process, and recycling difficulties. Identifying good additives or accelerators to improve the catalytic activities and stabilities of catalysts are the main tasks for future research.

3. Indirect synthetic process

Because of the major difficulties encountered in current methods for the direct synthesis of ethylene glycol from syngas,

Scheme 2. Reaction mechanism of direct synthesis of ethylene glycol from syngas.

Scheme 3. Reaction pathways for ethylene glycol production by carbonylation of formaldehyde.

indirect synthetic processes with relatively mild reaction conditions and good product selectivity have become the focus of research. The main methods of indirect synthesis include carbonylation of formaldehyde, CO coupling reactions, hydroformylation of formaldehyde, and condensation of formaldehyde. Carbonylation of formaldehyde and CO coupling reactions are considered to be the best prospects for industrialization.

3.1. Carbonylation of formaldehyde

In the early 1940s, DuPont developed the carbonylation of formaldehyde for the synthesis of ethylene glycol; the reaction pathway is shown in Scheme 3. Ethylene glycol was synthesized by catalytic hydrogenation of methyl glycolate, which was generated from the carbonylation and esterification of formaldehyde, an intermediate product prepared from syngas. All the raw materials used came from the coal chemical industry, so they had the advantages of being plentiful and cheap. So far, various catalytic systems have been developed, such as liquid acids, solid acids, metal-carbonyl complexes, and ionic liquids. DuPont [10] used concentrated H_2SO_4 or HCl to catalyze the formation of glycolic acid under reaction conditions of 150–225 °C/ $P_{\text{CO}} = 90$ MPa, followed by esterification with methanol to generate methyl glycolate. The methyl glycolate was further catalytically reduced using cupric chromite to produce ethylene glycol under conditions of 210–215 °C/ $P_{\text{H}_2} = 3.0$ MPa/space velocity 2000 h^{-1} . Although the total yield of ethylene glycol reached 90%, there were still some disadvantages such as harsh reaction conditions and consumption of large amounts of liquid acids, which caused environment pollution and apparatus corrosion.

In view of the disadvantages of DuPont's sulfuric acid method, such as serious corrosion and harsh reaction condition, Chevron Research [11,12] replaced H_2SO_4 by HF as the catalyst and obtained a 95% yield of methyl glycolate under relatively mild reaction conditions (50 °C and 6.9 MPa). Although it was claimed that the method solved the pollution problems, no example of its use in industrial production has been reported. Ethylene glycol was obtained in 96% yield by Cu–Cr-catalyzed hydrogenation of methyl glycolate under conditions of 205 °C/ $P_{\text{H}_2} = 3.15$ MPa/space velocity 2000 h^{-1} .

In 1976, Montedison [13] successfully developed $\text{Cu}(\text{CO})_3^+$ and $\text{Ag}(\text{CO})_2^+$ catalytic systems to catalyze carbonylation in a strong acid under relatively mild reaction conditions, although the carbonylation rate was slow. Souma et al. [14,15] found that $\text{Cu}(\text{CO})_3^+$ or $\text{Ag}(\text{CO})_2^+$ could catalyze carbonylation of formaldehyde in H_2SO_4 or BF_3 to give almost 100% yields under reaction conditions of 25 °C/ $P_{\text{CO}} = 1.0$ MPa. However, the reac-

Scheme 4. Reaction mechanism of $[\text{M}(\text{CO})_n]^+$ -catalyzed carbonylation of formaldehyde.

tion only proceeded with high concentrations of catalysts and acids; the concentrations of $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$ could not be lower than 0.2 mol/L and 0.4 mol/L, respectively. At the same time, the reaction did not proceed if the concentration of sulfuric acid was lower than 84.5% or the ratio of BF_3 and H_2O was less than 2. The proposed reaction mechanism is shown in Scheme 4. Formaldehyde was first protonated to a hydroxyl carbon cation, which further reacted with CO to generate a carbonyl carbon cation, using $[\text{Cu}(\text{CO})_n]^+$ or $[\text{Ag}(\text{CO})_2]^+$ as the catalyst. The carbonyl carbon cation could react with water to generate glycolic acid or with alcohol to form glycolate.

Since the 1980s, companies such as Mitsubishi Chemical and Hearst have successfully developed heterogeneous catalytic system consisting of heteropoly acids and ion-exchange resins. In 1983, Hendriksen et al. [16] reported Nafion-H-catalyzed carbonylation of formaldehyde using trioxane as the formaldehyde source and 1,4-dioxane as the solvent. Under reaction conditions of $\text{HCHO}:\text{H}_2\text{O}:\text{H}^+ = 10:10:1$ (molar ratio)/150 °C/ $P_{\text{CO}}(\text{rt}) = 18.6$ MPa, the conversion of formaldehyde reached 97% after reaction for 3 h, with 69% glycolic acid selectivity. Although this method resolved problems such as equipment corrosion and difficulties with catalyst separation, it still had the disadvantages of low product selectivity and high reaction pressure. Lee et al. [17] significantly improved the product selectivity by using polystyrene sulfonic acid resins as the catalyst (see Table 1). For instance, methyl glycolate was obtained in 85% yield after reaction for 2 h, using Amberlyst 15 as the catalyst and 1,4-dioxane as the solvent, under condition of 135 °C/ $P_{\text{CO}} = 24.1$ MPa. The Amberlyst 15 could be reused 10 times without a reduction in the catalytic activity. As well as the formation of the intermediate HOCH_2CO^+ from the reaction of formaldehyde and CO in the acidic system, it was considered that self-condensation of formaldehyde, generating methyl formate and paraformaldehyde, would reduce the product selectivity (shown in Scheme 5). A high CO pressure was there-

Table 1
Carbonylation of formaldehyde over polystyrenesulfonic acid resins.

Catalyst	HCHO reacted: H^+ (molar ratio)	HCHO reacted:cat (10^{-2} mol/g)	Selectivity (%)
Nafion NR-50	15.9	1.272	81.6
Amberlyst 36	5.4	2.538	87.9
Amberlyst 15 (wet)	5.2	2.444	79.6
Amberlyst 15	3.9	1.833	61.9
Amberlyst XN-1010	4.5	1.485	58.9
Dowex 50×8-100	4.5	2.295	88.9
Dowex 50×8-400	4.4	2.271	85.1

Conditions: 4 g catalyst, 135 °C, $P_{\text{CO}} = 24.1$ MPa, 1 h, $\text{H}_2\text{O}:\text{HCHO} = 1$ (molar ratio).

Scheme 5. Reaction pathways of acid-catalyzed carbonylation of formaldehyde.

fore important in improving the product selectivity.

In 2011, Barri et al. [18] reported zeolite-catalyzed carbonylation of formaldehyde under anhydrous conditions; the results are shown in Table 2. The selectivity for methyl glycolate reached 99.6% using ZSM-5 as a catalyst (20 wt% of formaldehyde) under reaction conditions of 200 °C/ P_{CO} (rt) = 8.0 MPa for 2 h. The selectivity obtained using ZSM-5 as the catalyst was better than those obtained using a heteropoly acid (HPW 77.5%) or an ion-exchange resin (Amberlyst-15 62.9%). Because of the low catalytic activity of the zeolite, the yield of methyl glycolate was only 47.7%. A mechanism of formaldehyde carbonylation under anhydrous conditions was proposed based on reported research (shown in Scheme 6). Formaldehyde reacts with CO under the mediation of a solid acid, H^+S^- , to form 1,4-dioxan-2,5-dione or a linear polymer, followed by esterification with methanol to generate methyl glycolate.

In 2009, Sun et al. [19] developed a heteropoly acid catalytic system; the results are shown in Table 3. The yield of methyl glycolate reached 89.3% after reaction for 4 h, using tetramethylene sulfone as the solvent and conditions of $HCHO:H_2O:H_3PW_{12}O_{40} = 19:19:1$ (molar ratio)/120 °C/ P_{CO} (rt) = 4.0 MPa. The raw materials and products could be separated by vacuum distillation, which enabled the reuse of the catalysts and solvents. Although the conversion of formaldehyde was unchanged, the selectivity for methyl glycolate decreased gradually with catalyst reuse. The reaction conditions were comparatively mild, but the amount of catalyst used was five

Table 2
Carbonylation of formaldehyde with zeolite catalysts.

Catalyst	Catalyst:CH ₂ O (wt%)	Temperature (°C)	Yield (%)		
			MG	DMDG	MMAc
ZSM-5(55)	20	200	47.7	<0.1	<0.1
ZSM-5(280)	20	180	18.4	0.4	<0.1
Y(30)	20	180	27.8	<0.1	1.9
Y(5)	20	180	1.8	<0.1	1.2
HPW	23	140	65.1	33.7	<0.1
Amberlyst-15	40	180	68.6	19.8	<0.1
Amberlyst-70	67	180	53.5	31.4	<0.1

MG: methyl glycolate; DMDG: dimethyl diglycolate; MMAc: methyl methoxy acetate.

Scheme 6. Reaction pathways for carbonylation of formaldehyde under anhydrous conditions.

Table 3
Catalytic activities of different HPAs in carbonylation of formaldehyde.

HPA(Keggin)	pK ₁ (acetone)	MG yield (%)
H ₃ PW ₁₂ O ₄₀	1.6	89.3
H ₄ SiW ₁₂ O ₄₀	2.0	89.0
H ₃ PMo ₁₂ O ₄₀	2.0	65.0
H ₄ SiMo ₁₂ O ₄₀	2.1	39.8

times more than that of the formaldehyde mass.

Li and co-workers [20,21] found that using an ionic liquid, [BMIm]PF₆ or [BMIm]BF₄, as the solvent and *p*-TsOH (Ts: tosyl, CH₃C₆H₄SO₂) as the catalyst and a transition-metal compound (such as CF₃SO₃Ag) as a co-catalyst, under conditions of *p*-TsOH:CF₃SO₃Ag:HCHO:H₂O = 100:1:202:202 (molar ratio)/135 °C/ P_{CO} (rt) = 10 MPa, the yield of methyl glycolate obtained was 86.7% after reaction for 2 h. This yield was higher than that achieved in an organic solvent under the same conditions (see Table 4). However, there were still disadvantages such as a complicated catalytic system, use of a large amount of ionic liquid, and decreased ionic liquid flowability on reuse.

In 2012, Song et al. [22] reported functionalized acidic ionic liquid (BAIL)-catalyzed carbonylation of formaldehyde, with a methyl glycolate yield of 97.6% (see Table 5) after reaction for 8 h, using trioxane as the formaldehyde source and tetramethylene sulfone as the solvent, under conditions of H₂O:HCHO:BAIL = 10:5:2 (molar ratio)/170 °C/ P_{CO} (rt) = 5.0 MPa. The reaction activity was not obviously reduced even after reuse of the catalyst and solvent eight times. The acidic ionic liquid solved some of the problems such as serious corrosion by liquid acids, environmental pollution, and catalyst reusability. It also overcame some of the difficulties associated with using solid acid catalysts, such as large amounts of catalysts, low catalytic activity, and catalyst coking. The proposed mechanism of acidic-ionic-liquid-catalyzed carbonylation of formaldehyde is shown in Scheme 7. In the first step, trioxane dissociated to formaldehyde under acidic conditions; in the second step, formaldehyde was protonated to a hydroxyl carbon cation under the mediation of the ionic liquid, followed by carbonylation of CO to a carbonyl carbon cation, which reacted with water to form glycolic acid.

Table 4
Carbonylation of formaldehyde catalyzed by *p*-TsOH in ionic liquid.

Metal complex	Solvent	HCHO conversion (%)	Yield (%)			Selectivity (%)
			MG	MF	MMAc	
—	MB	93.8	59.8	6.3	5.2	63.8
CF ₃ SO ₃ Ag	MB	93.6	59.3	1.7	4.2	63.4
CF ₃ SO ₃ Ag	[BMIm]BF ₄	93.2	49.7	4.8	1.5	53.3
—	[BMIm]PF ₆	99.0	71.7	1.4	0.6	72.4
CF ₃ SO ₃ Ag	[BMIm]PF ₆	99.5	86.7	1.8	0.7	87.1
AgBF ₄	[BMIm]PF ₆	99.6	83.3	0.6	1.3	83.6
Ag ₂ SO ₄	[BMIm]PF ₆	99.4	81.0	1.7	1.0	81.5
CH ₃ COOAg	[BMIm]PF ₆	99.3	79.3	1.8	1.2	79.9
(CH ₃ COO) ₂ Pd	[BMIm]PF ₆	99.7	75.2	3.3	2.9	75.4
(CF ₃ SO ₃) ₂ Cu	[BMIm]PF ₆	97.8	80.8	2.5	0.5	82.6

MB: methyl benzoate; MF: methyl formate; [BMIm]BF₄: 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIm]PF₆: 1-butyl-3-methylimidazolium hexafluorophosphate.

Catalytic activities of different acidic ionic liquids in carbonylation of formaldehyde.

IL1: R = CH ₃ ,	<i>n</i> = 3, X = CH ₃ SO ₃
IL2: R = CH ₃ ,	<i>n</i> = 4, X = CH ₃ SO ₃
IL3: R = (CH ₂) ₃ CH ₃ ,	<i>n</i> = 4, X = CH ₃ SO ₃
IL4: R = CH ₃ ,	<i>n</i> = 4, X = HSO ₄
IL5: R = CH ₃ ,	<i>n</i> = 4, X = <i>p</i> -(CH ₃)C ₆ H ₄ SO ₃

ILs	HCHO conversion (%)	Yield (%)			Selectivity for MG (%)
		MG	MMAc	MF	
IL1	98.9	96.4	1.5	0.02	97.4
IL2	99.3	97.6	1.0	0.6	98.3
IL3	97.9	82.3	15.3	0.3	84.1
IL4	90.2	85.2	2.6	0.01	92.6
IL5	76.3	73.6	0.1	2.6	92.8
<i>p</i> -TsOH	38.3	36.1	1.2	1.0	94.1

To develop the C1 chemical industry and to meet the demands for raw materials of the polyester industry, research has been conducted on non-petroleum-based novel technologies for the synthesis of ethylene glycol using coal-based formaldehyde and syngas, which will complement or replace the current petroleum-based route. The industrialization of this technology is beneficial in improving the efficiency of coal and syngas, optimizing the coal-chemical industries link, and compensating for the shortage of polyester raw materials in China.

3.2. CO coupling method (dialkyl oxalate method)

In 1968, Unocal Corporation [23–25] proposed a route for

Scheme 7. Proposed reaction mechanism of carbonylation of formaldehyde catalyzed by ionic liquids.

synthesizing ethylene glycol via CO coupling (Eq. (2)) using cheap starting materials such as NO, CO, O₂, alcohols, and H₂. The process involved making nitrites from the reaction between an alcohol and N₂O₃, and then coupling with CO catalyzed by PdCl₂-CuCl₂ to obtain dialkyl oxalate, which was further catalytically hydrogenated to ethylene glycol. Under conditions of 125 °C/7.0 MPa, the selectivity for oxalic ester was only 66%. The reaction process did not actually consume any alcohols and nitriles; only CO, O₂, and H₂ participated in the synthesis of ethylene glycol (Eq. (3)). Many by-products, including dialkyl carbonate, CH₃COOR, and CO₂, were generated in this process, which caused a low yield of ethylene glycol. The halogen-containing catalysts would severely damage the equipment. The use of a large amount of dehydrator to keep the reaction system under anhydrous conditions decreased the economy of the overall process. Acro and UBE [26] improved the catalytic system by adding CO group 3rd alkali-metal salts (LiCl, Na₂CO₃, NaOAc, etc.), ammonium/trialkylamine, and sulfate. Although the modified method no longer required dehydrators, equipment corrosion still occurred. Fang et al. [27] used K₂CO₃ as an accelerator in the reaction, obtaining 18.0% ethanol conversion and 79.6% total selectivity for diethyl oxalate and diethyl carbonate.

In 1978, UBE and UCC introduced nitrites into the reaction system and thus solved the serious corrosion problems which occurred in the Unocal method [28–30]. The oxalate yield reached 98% for the 2% Pd/C-catalyzed coupling reaction of CO and butanol, in the co-presence of nitrite, under conditions of 90 °C/9.8 MPa. Currently, there are still some drawbacks to liquid reaction systems, such as slow reaction rates, too many by-products, and catalyst loss.

To solve the problems of the liquid-phase method, such as harsh reaction conditions and a slow reaction rate, UBE [31] developed a gas-phase method via gas-phase hydrogenation of dialkyl oxalate, which was generated by the reaction of CO and methyl nitrite or ethyl nitrite. The by-products, NO and O₂, could react with methanol to generate RONO, enabling recycling. The yield of dimethyl oxalate reached 54.7% using Pd/Al₂O₃ as the catalyst under reaction conditions of 104–117 °C/0.2 MPa. A bench-scale trial of the process was successfully run for 480 h with a 432 g/(L·h) average space time yield, achieving continuous catalytic cycles and reuse of the NO by-product. The gas-phase process has the advantages of high selectivity, mild reaction conditions, and no use of solvent. Compared with the liquid-phase method, the gas-phase method is more economical.

From the 1980s, China started research on the synthesis of oxalate and its derivatives by CO coupling reactions. Research on catalysts focused on Pd loaded on α -Al₂O₃ with different co-catalysts; the catalytic activities of different catalysts are listed in Table 6. The Fujian Institute of Research on the Struc-

Table 6

Oxalate synthesis by gas-phase catalytic coupling of CO.

Organiza- tion	Catalyst	Tempera- ture (°C)	Conver- sion (%)	Selectivi- ty (%)	Refer- ence
FIRSM	Pd/ α -Al ₂ O ₃	160	65.9	>95	[32–34]
ECUST	Pd-Ce/ α -Al ₂ O ₃	140	78		[35,36]
Tianjin Uni.	Pd-Fe/ α -Al ₂ O ₃	110	40–50	>96	[37–42]
Tianjin Uni.	Pd-Ti-Ce/ α -Al ₂ O ₃	120	30–58	>96	
Zhejiang Uni.	Pd-Ga/ α -Al ₂ O ₃	100–110	35–55	85	[43]
Nankai Uni.	Pd-Fe-La/ δ -Al ₂ O ₃	110–130			[44]
ECUST	Pd/Nano-carbon-fiber	80–140	>85	100	[45]

ture of Matter (FIRSM) [32–34] achieved a 750 g/(L·h) average space time yield using 20% Pd/ α -Al₂O₃ as the catalyst under conditions of 120–175 °C/atmospheric pressure/3000 h⁻¹, and started a pilot trial. Zhao and co-workers [35,36] at the East China University of Science and Technology (ECUST) achieved a space time yield of dimethyl oxalate of 821 g/(L·h) via Pd-Ce/ α -Al₂O₃-catalyzed-coupling of CO with methyl nitrite at 140 °C, with 78% conversion of CO per pass. They found that increasing the specific surface area, pore radius, or volume of the support improved the catalytic activity. A co-catalyst dispersed Pd more efficiently and reduced the Pd particle size, and thus increased the conversion of CH₃ONO to 84.7% from 57.1%. Ma and co-workers at Tianjin University [37–42] prepared a supported Pd-Fe/Al₂O₃ bimetallic catalyst (Pd 1.5%, Fe 0.9%) and achieved a 408–670 g/(L·h) space time yield of diethyl oxalate under conditions of 110 °C/0.1 MPa, and a residence time of 2–3 s, with 32% conversion of CO per pass. Jiang at Zhejiang University [43] developed a Pd-Ga/ α -Al₂O₃ catalytic system that gave 33–55% conversion of CO per pass and 85% diethyl oxalate selectivity. Guo et al. at Nankai University [44] used a Pd-Fe-La/ δ -Al₂O₃ multicomponent catalytic system in a fixed bed at 100–130 °C with a residence time of 0.5–3 s, obtaining an average yield of 3.29 g/(g·h). Zhao and co-workers at ECUST [45] explored a new type of nanocarbon-fiber-supported catalyst for CO coupling reactions and achieved over 85% conversion of dimethyl oxalate per pass and almost 100% product selectivity.

Chen et al. [33] investigated the mechanism of CO coupling to oxalate (Scheme 8). They proposed a nucleophilic reaction mechanism. Under the reaction conditions used, an active Pd⁰ center coordinated with two CO molecules to form a Pd-carbonyl complex, which was prone to nucleophilic attack by RO⁻ since the interaction between the support and Pd made the Pd center more negative. Following oxidative addition with RO-NO⁺, a dialkoxy-carbonyl-Pd complex was formed, which could further release two NO molecules. Oxalate was generated after reductive elimination, with regeneration of Pd⁰. In this reaction, the coordination of two molecules of RO-NO⁺ with the same active center was a secondary reaction, which was identical to the reaction order using nitrites. Meng et al. [46] studied the kinetics of a Pd-Fe/ α -Al₂O₃-catalyzed CO coupling reaction for preparing diethyl oxalate. They believed that the EtO-NO bond had a low dissociation energy and could be easily cleaved to give EtO⁻ and NO, which were adsorbed on the active sites of

Scheme 8. Mechanism of oxalate synthesis via coupling of CO with RONO.

the catalyst with a balance. The rate-determining step was therefore the surface reaction. They also investigated the effect of hydrogen on the reaction and found that hydrogen could react with EtO⁻ to form ethanol.

Song et al. [47,48] studied the mechanism of the CO coupling reaction using in situ Fourier-transform infrared spectroscopy and found that CO was adsorbed on a Pd active center in both linear and bridging configurations. CO reacted with a Pd²⁺-alkoxy complex to form a Pd²⁺-dialkyl-carbonyl complex, which further coupled to give oxalate, with the reduction of Pd²⁺ to Pd⁰. In other words, the active Pd component underwent an oxidation–reduction process in a CO gas-phase coupling reaction to produce oxalates (Scheme 9), and the adsorption and transformation of CO were the rate-determining steps.

Wang et al. [49] confirmed that the CO coupling reaction followed a “co-catalytic cycle” secondary reaction pattern (Scheme 10). Pd⁰ was successively oxidized to the active intermediates Pd⁺OC₂H₅ and Pd²⁺(OC₂H₅)₂ by ethyl nitrite. The linear CO adsorbed on the catalyst surface was easily inserted into Pd²⁺-alkoxy compounds to form Pd²⁺-dialkyl-carbonyl complexes. Reductive elimination to form diethyl oxalate and Pd⁰ for the next catalytic cycle could only occur if the Pd²⁺-dialkyl-carbonyl complexes on the catalyst surface had enough space (no hindrance). The valence state of Pd was changed by the reaction of ethyl nitrite and CO; the transformations of catalyst intermediates and the oxidation–reduction process all followed the “co-catalytic cycle” mechanism.

Scheme 9. Reaction mechanism of CO coupling to oxalate in gas phase.

Scheme 10. Reaction scheme for catalyst cycling.

Lin et al. [50] believed that the CO coupling reaction occurred between the CO in the bridge adsorbed state and gaseous methyl nitrite, with adsorption of CO as the reaction-controlling step. Because of the strong electronegativity of oxygen in CO, the carbon in CO was more positive and was easily nucleophilically attacked by the CH_3O^- of $\text{CH}_3\text{O}-\text{NO}^+$. NO^+ bonded with the electrons on the outer sphere of Pd to form stable NO in a linear adsorbed state, and immediately formed intermediate Pd^{2+} -dialkyl-carbonyl complexes, which could give dimethyl oxalate via reductive elimination (Eq. (4)).

Chen et al. [51] reported the synthesis of dialkyl oxalates by coupling CO and nitrites in a $\text{Pd}(\text{acac})-\text{PPh}_3$ catalytic system. Under conditions of $60^\circ\text{C}/P_{\text{CO}} = 3.0 \text{ MPa}$ with a molar ratio of $\text{PPh}_3/\text{Pd}(\text{acac})_2 = 3$, the catalytic activity reached $8.3 \text{ mol}/(\text{mol}\cdot\text{h})$. In the reaction process, the acac ligand of the pre-catalyst $\text{Pd}(\text{acac})_2$ was replaced by PPh_3 to give $[(\text{PPh}_3)_3\text{Pd}]$, which then coordinated with CO to form $(\text{PPh}_3)_3\text{Pd}(\text{CO})$. As a result of coordination of CO and Pd, their bond resonance energies were sufficiently similar enough to promote the transformation $\text{Pd}-\text{C}(\text{sp}) \leftrightarrow \text{Pd}-\text{C}(\text{sp}^2)$ to generate an $[\text{L}_3\text{Pd}=\text{C}=\text{O}]$ complex, in which the carbonyl carbon was prone to nucleophilic attack by RO^- of $\text{RO}-\text{N}=\text{O}$ to form an alkoxy-carbonyl complex, followed by reductive elimination to produce oxalate (Scheme 11).

Currently, the use of CO coupling reactions to prepare ethylene glycol is limited because further development of the catalytic hydrogenation of dialkyl oxalate is needed. Many companies and institutes are investigating this process, and some

 Scheme 11. Mechanism of CO coupling with RONO, catalyzed by $\text{Pd}(\text{acac})_2$.

catalytic systems have been reported. In the 1980s, Matteoli et al. [52,53] reported noble-metal-catalyzed homogeneous hydrogenation of oxalates. Using $\text{Ru}(\text{CO})_2(\text{CH}_3\text{COO})_2(\text{P}^i\text{Bu}_3)_2$ as the catalyst, under conditions of $180^\circ\text{C}/P_{\text{H}_2}(\text{rt}) = 20.0 \text{ MPa}$, the selectivity for ethylene glycol reached 82%. Ru catalysts have outstanding catalytic capacities, but their disadvantages such as high costs, preparation difficulties, short lifetimes, and difficulties in catalyst separation, have restricted their industrial applications.

In 1987, ARCO [54] developed Cu-Cr-catalyzed hydrogenation of oxalates. The reaction proceeded under a pressure of 3.0 MPa, to give an ethylene glycol yield of 95%. However, because of serious environmental contamination and difficulties in recycling Cr, development of this approach is unlikely. UCC used Cu/SiO₂ to catalyze the hydrogenation of dimethyl oxalate under conditions of $180\text{--}240^\circ\text{C}/3.0 \text{ MPa}$, with a molar ratio of hydrogen/oxalate = 67, and obtained nearly 100% conversion of dimethyl oxalate and 97% ethylene glycol selectivity. In 1994, Engelhard [55] reported a catalytic system consisting of Cu-Zn oxides and a small amount of Al₂O₃; the system had good catalytic performance.

In China, research on hydrogenation of ethylene glycol has focused on gas-phase methods; the performances of various catalysts are shown in Table 7. Researchers at the FIRSM [56] used a supported Cu-Cr/SiO₂ catalyst to catalyze the hydrogenation of diethyl oxalate under conditions of $205\text{--}240^\circ\text{C}/2.5\text{--}3.0 \text{ MPa}$, with a molar ratio of hydrogen/oxalate = 60, and obtained 99.8% conversion of diethyl oxalate and 95.3% ethylene glycol selectivity. Researchers at Tianjin University [57] used a Cu-Zn/SiO₂ catalyst to catalyze the hydrogenation of diethyl oxalate under conditions of $200\text{--}250^\circ\text{C}/3.0 \text{ MPa}$, with a molar ratio of hydrogen/oxalate = 30–100, and obtained 95% conversion of diethyl oxalate and 80% ethylene glycol selectivity. Li and co-workers at ECUST [58,59] studied a

Table 7

Preparation of ethylene glycol by catalytic hydrogenation of oxalate esters.

Organization	Catalyst	Temperature ($^\circ\text{C}$)	Pressure (MPa)	Conversion (%)	Selectivity (%)	Reference
FIRSM	Cu/Cr/SiO ₂	208–230	2.5–3.0	99.8	95.3	[56]
Tianjin University	Cu-Zn/SiO ₂	220	3.0	95.0	>90.0	[57]
ECUST	Cu/SiO ₂	205	2.5	100	99.1	[58,59]

Reaction conditions: [Rh] = 0.02 mol, [HCHO] = 2 mol (paraformaldehyde), 110 °C, 13.5 MPa (CO:H₂ = 1:1), 2 h; ^a *T* = 140 °C, [HCHO] = 2.9 mol (37% aqueous formaldehyde); ^b Including 1.6% of ethylene glycol.

Scheme 12. Mechanism of hydroformylation of formaldehyde.

method. The cost of the raw materials is high, and formaldehyde can easily be reduced to methanol, which further condenses with formaldehyde. Because Rh catalysts are expensive, it is important to develop reusable catalysts and to explore non-Rh catalytic systems.

3.4. Condensation of formaldehyde method

Other indirect methods for the synthesis of ethylene glycol include condensation of formaldehyde and formaldehyde electrochemical hydrogenation dimerization, but these are currently at the stage of small-scale trials.

Weiss et al. used a zeolite catalyst and 30% formaldehyde aqueous solution as the raw material to prepare hydroxyacetaldehyde in NaOH solution, followed by Ni-catalyzed hydrogenation, to produce ethylene glycol under conditions of 94 °C/atmospheric pressure/space velocity = 1.21 h⁻¹ (Eq. (8)). The development of hydrogenation techniques is slow at present [8].

Sanderson et al. [72–74] reported that 1,3-dioxolane reacted with formaldehyde in the presence of a free radical initiator, $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$, to produce 2-(hydroxymethyl)-1,3-dioxolane, which was catalytically hydrogenated to ethylene glycol (Eq. (9)). The selectivity for ethylene glycol increased with decreasing reaction temperature. The selectivity for ethylene glycol was 44.9% at 75 °C.

In 1984, SKA Associates [75,76] developed formaldehyde electrochemical hydrogenation dimerization for the synthesis of ethylene glycol using a formaldehyde–water solution as the raw material, and controlling the pH of the electrolyte at 4.4 by adding formic acid in an aqueous sodium formate solution. In 1991, Weiberg [77] achieved efficient inhibition of side reactions, with 90% ethylene glycol selectivity and yield, using a graphite electrode (Ultracarbon ST-50) at 80–90 °C in an electrolyte of pH 4.4. The ethylene glycol selectivity and yield even

reached 99% under optimized conditions. The reaction conditions are mild, but high electricity consumption and low product concentration are disadvantages.

4. Summary

Because of the high price of oil and the shortage of crude oil, it is importance to develop basic and practical research for the CO industry, based on the relatively abundant coal resources in China. In particular, with respect to national energy security and a diversified industrial structure, this could provide a new model for development of the coal industry by integrating gas, power generation, and chemical engineering in a high-efficiency energy and chemical engineering system. The synthesis of ethylene glycol from coal and syngas is of great significance in advancing the development of the coal chemical industry, supplementing the low oil and gas resources in China, compensating for the shortage of polyester raw materials in China, safeguarding energy security, and promoting sustainable development of the economy.

A breakthrough in the direct synthesis of ethylene glycol from syngas will be highly important because this is an atom economic reaction; the reaction conditions are currently too harsh for industrial production. The carbonylation of formaldehyde has advantages with respect to sources and prices of the starting materials. Environmentally friendly and reusable ionic liquid catalytic systems have been developed to overcome the defects in traditional systems, such as the difficulty of separating liquid acids and serious corrosion of equipment. These reactions are therefore promising. The CO coupling method has been used on a pilot-plant scale in China. The reaction conditions are relatively mild, but there are several drawbacks, including complicated starting materials, the use of precious-metal catalysts, high cost, long process time, and equipment corrosion by the nitric acid formed from by-produced water and nitrogen oxides. The cost of the hydroformylation of formaldehyde using trioxane or paraformaldehyde as the formaldehyde source and the noble-metal rhodium as the catalyst is high. The condensation of formaldehyde is another attractive route as it uses mild reaction conditions and gives high selectivity and yield.

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Graphical Abstract

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Progress in synthesis of ethylene glycol through C₁ chemical industry routes

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Ethylene glycol (EG) is an important industrial chemicals and especially it could be used to synthesize polyester resins and fibers. The pertinent literatures on EG synthesis through C₁ chemical industry routes are summarized.

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碳一化工路线制备乙二醇研究进展

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摘要: 乙二醇(EG)是一种重要的化工原料,主要用来生产新型聚酯纤维.近年来由于我国聚酯产业发展迅速,极大的推动了对乙二醇的需求.碳一化工路线以资源丰富、价格便宜的天然气或煤为原料合成乙二醇,有着诱人的工业化前景.综述了以合成气为原料合成乙二醇的研究进展,包括合成气直接合成法、甲醛羰化法、CO偶联法、甲醛氢甲酰化法以及甲醛缩合法等.

关键词: 碳一化工; 乙二醇; 合成气; 甲醛; 羰基化; 氧化偶联; 氢甲酰化

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1. 前言

世界能源需求和结构状况的矛盾迫使人们积极开发石油替代品及其衍生物,天然气和煤经合成气等碳一化工过程合成有机化工原料是解决供需矛盾的重要措施之一.我国是世界上最大的煤炭生产国,煤炭在已探明的一次性能源结构中占96%,有超过75%的煤炭仅作为低效益燃料使用,发展碳一化工已成为我国减少煤炭行业重污染、发展清洁有机原料技术的重要组成部分.乙二醇是一种重要的有机化工原料,主要用来生产聚酯纤维、防冻剂、不饱和聚酯树脂、增塑剂、表面活性剂等.此外,乙二醇在烟草、纺织、化妆品等工业也有广泛的用途.我国是世界最大的乙二醇消费国,90%乙二醇用来生产聚酯.近年来由于我国聚酯产业发展迅速,极大推动了对乙二醇的需求,但我国乙二醇生产能力不足,产品进口量逐年上升,供需矛盾越来越突出^[1].据报道,2010年我国乙二醇的消费量为913.9万吨,自给率只有27.4%,预计我国乙二醇需求量将以年均7.2%的速度增长,到2014年达到1100.0万吨.

目前,工业上生产乙二醇主要采取从乙烯出发的环氧乙烷直接水合法.该方法反应产物含水量高,后续设备流程长、能耗高、收率低.20世纪70年代以来,由于石油资源不断匮乏,人们试图寻求以资源丰富、价格便宜

的天然气或煤代替石油制取乙二醇,并取得了很大的进展.从合成气出发制备乙二醇工艺路线主要有直接工艺和间接工艺,工艺路线如图式1所示.直接工艺即由合成气直接合成乙二醇;间接工艺是合成气经甲醇、甲醛等中间化合物后再转化为乙二醇,主要有甲醛羰化法(羰基乙酸法)、CO偶联法(草酸酯法)、甲醛氢甲酰化法以及甲醛缩合法等.

2. 直接合成工艺

从反应方程式上看(见式(1)),由合成气直接制备乙二醇是“原子经济反应”,原料利用率高.陈红萍等^[2]对该反应热力学进行了分析,发现低于81.5°C时, $\Delta_r G_m < 0$,热力学上较易进行,但反应速率较低,需要开发高活性催化剂.高压有利于推动平衡向产物方向转移,但过高压力使生产投资费用增加.

1948年,DuPont公司^[3]首次提出由合成气直接合成乙二醇的方法,采用 $\text{Co}_2(\text{CO})_8$ 为催化剂,反应在304 MPa的高压下进行,反应条件苛刻,乙二醇收率低,难以满足工业化生产的要求.20世纪70年代,UCC公司^[4,5]报道了以羰基铑配合物为催化剂,在四氢呋喃、甲醇、异丙醇等有机溶剂中从合成气制备乙二醇.催化剂不稳定且活性低,高压和选择性低的问题仍未解决.随后,UCC公司^[6]使用大体积烷基膦和胺改性的羰基铑为催化剂,以

四甘醇二甲醚为反应溶剂,其催化活性和选择性明显提高.反应可在230 °C, 49.0 MPa, $n(\text{H}_2)/n(\text{CO}) = 1$ 的条件下进行,乙二醇选择性为67%,时空收率达到了259 g/(L·h),副产物为丙二醇、甘油和甲醇.但是合成气整体转化率和产物选择性仍比较低.

1987年, Murata等^[7]报道了一种咪唑改性的钌系催化剂,研究发现咪唑类化合物的强配位作用和碱性作用对反应有利,采用 $\text{Ru}_3(\text{CO})_{12}$ 、苯并咪唑盐和三乙胺的催化剂体系,在150 °C和10 MPa条件下反应3 h,可得41.3%的乙二醇,反应条件相对温和. Mitsui Chemicals公司和Sumitomo Chemical公司^[8]以Ru-1-烷基-2-取代苯并咪唑为催化剂,在四甘醇二甲醚溶剂中获得了很高的催化活性和选择性(70%).增加咪唑及其衍生物的浓度,催化剂活性明显提高,但催化体系在反应条件下不稳定,引起N-甲基苯并咪唑分解而造成损失.

Masuda等^[9]研究了合成气直接合成乙二醇反应机理,发现随氢分压的升高乙二醇选择性显著增加,而副产物甲醇选择性明显降低,甲酸甲酯的选择性几乎不变;但产物选择性几乎不受CO分压的影响.因而认为, HCHO是反应中间体,其生成过程和形态决定了反应活性和产物选择性(见图式2).

目前,由合成气直接合成乙二醇仍处于研究阶段,存在反应条件苛刻,催化剂稳定性差,分离困难及难以循环使用等问题,离工业化仍有相当的距离.研究的重点在于寻求优良的助剂或促进剂,以期提高催化剂的活性和稳定性.

3. 间接合成工艺

由于直接法合成乙二醇的难度大,因此反应条件相对温和、选择性高的间接工艺路线成为目前研究的热点.通过合成气间接合成乙二醇的方法主要有:甲醛羰基化法、CO偶联法、甲醛氢甲酰化法和甲醛缩合法等.其中甲醛羰基化法和CO偶联法被认为最具有工业化前景.

3.1. 甲醛羰基化法

20世纪40年代初, DuPont公司开发了甲醛羰基化法制备乙二醇的技术,该路线如图式3所示,以甲醛和合成气为反应原料,甲醛羰基化、酯化合成乙醇酸甲酯,后者催化加氢生产乙二醇.原料均来自煤,存在资源和价格优势.迄今为止,已发展了包括液体酸、固体酸、金属羰基物、离子液体等多种催化剂体系. DuPont公司^[10]采用浓 H_2SO_4 或HCl为催化剂,在150~225 °C和 $P_{\text{CO}} = 90$ MPa下反应生成乙醇酸,然后经甲醇酯化为乙醇酸甲酯,后者在

210~215 °C, $P_{\text{H}_2} = 3.0$ MPa, 空速2000 h^{-1} 的条件下,用亚铬铜催化还原生成乙二醇.乙二醇的总收率可达90%,但存在反应条件苛刻,液体酸用量大,造成环境污染及设备腐蚀等缺陷.

鉴于DuPont公司硫酸法腐蚀严重、反应条件苛刻, Chevron Research公司^[11,12]使用HF代替 H_2SO_4 作催化剂,在较温和的条件下(50 °C, 6.9 MPa)反应,乙醇酸甲酯的收率为95%,据称可解决污染问题,但未见工业化生产报道.氢化反应采用Cu-Cr催化剂,在205 °C, $P_{\text{H}_2} = 3.15$ MPa和空速2000 h^{-1} 条件下反应,乙二醇收率可达96%.

Montedison公司^[13]于1976年开发成功了以羰基金属化合物 $\text{Cu}(\text{CO})_3^+$ 或 $\text{Ag}(\text{CO})_3^+$ 为主催化剂,在强酸体系中进行羰基化反应,反应条件相对缓和,但其羰基化速度较慢. Souma等^[14,15]系统考察了在 H_2SO_4 或 BF_3 体系中 $[\text{Cu}(\text{CO})_n]^+$ 或 $[\text{Ag}(\text{CO})_2]^+$ 催化的甲醛羰基化反应,在25 °C和 $P_{\text{CO}} = 1.0$ MPa下反应,甲醛转化率几乎达到了100%.但是反应需要在较高的催化剂浓度和酸浓度下进行: Cu(I)或Ag(I)的浓度分别不低于0.2和0.4 mol/L;在硫酸浓度<84.5%或 $\text{BF}_3 \cdot \text{H}_2\text{O} < 2$ 的条件下,反应几乎不会发生.他们对反应机理进行了推断,如图式4所示.甲醛首先质子化生成羟基碳正离子,羟基碳正离子再经 $[\text{Cu}(\text{CO})_n]^+$ 或 $[\text{Ag}(\text{CO})_2]^+$ 催化与CO反应生成羰基碳正离子;后者与水反应生成乙醇酸,或与醇反应生成乙醇酸酯.

20世纪80年代以来, Mitsubishi Chemical和Hearst等公司相继发展了以杂多酸、离子交换树脂为代表的多相催化剂体系. 1983年, Hendriksen等^[16]报道了全氟磺酸基树脂“Nafion-H”催化的甲醛羰基化反应,以三聚甲醛作为甲醛供体,二氧六环为反应溶剂,在 $\text{HCHO}:\text{H}_2\text{O}:\text{H}^+ = 10:10:1$ (mol ratio), 150 °C, P_{CO} (r.t.) = 18.6 MPa下反应3 h,甲醛转化率为96%,乙醇酸选择性为69%.该催化过程解决了设备腐蚀、催化剂分离困难等问题,但还是存在产物选择性低、反应压力高等缺陷. Lee等^[17]采用聚苯乙烯磺酸树脂为催化剂(见表1),产物选择性明显提高,以Amberlyst 15为催化剂,以1,4-二氧六环为溶剂,在135 °C和 $P_{\text{CO}} = 24.1$ MPa条件下反应2 h,乙醇酸甲酯收率最高可达85%,催化剂重复使用10次,活性未见下降.他们认为,在酸性体系中甲醛和CO反应除了生成中间体 HOCH_2CO^+ 外,甲醛自身发生缩合反应生成甲酸甲酯和多聚甲醛,降低了产物选择性,所以增加CO的压力是提高产物选择性的关键(见图式5).

2011年, Barri等^[18]报道了无水条件下沸石催化甲醛

羰基化反应,如表2所列.当以ZSM-5为催化剂(投料量为HCHO质量的20%),在200 °C, P_{CO} (r.t.) = 8.0 MPa下反应2 h,乙醇酸甲酯的选择性达99.6%,同等条件下好于杂多酸(HPW, 77.5%)和离子交换树脂(Amberlyst-15, 62.9%).但沸石催化活性较低,乙醇酸甲酯的收率只有47.7%.他们在前人研究的基础上,对无水条件下甲醛羰基化反应机理进行了推测,如图式6所示.甲醛首先在固体酸 H^+S^- 的作用下,与CO反应生成了反应中间体1,4-二氧六环-2,5-二酮或链状聚合物,然后经甲醇酯化为乙醇酸甲酯.

2009年, Sun等^[19]报道了杂多酸催化剂体系用于甲醛羰基化反应,结果见表3.可以看出,采用环丁砜为溶剂,在 $\text{HCHO}:\text{H}_2\text{O}:\text{H}_3\text{PW}_{12}\text{O}_{40}=19:19:1$ (摩尔比), 120 °C, P_{CO} (r.t.) = 4.0 MPa下反应4 h,乙醇酸甲酯收率达89.3%.减压蒸馏分离反应原料和产物,实现了催化剂和溶剂的重复使用.在重复使用过程中,甲醛转化率基本保持不变,乙醇酸甲酯选择性逐渐降低.该催化剂体系反应条件比较温和,但催化剂用量很大,其投料量为甲醛质量的5倍.

李涛等^[20,21]在离子液体[BmIm]PF₆或[BmIm]BF₄反应体系中,以甲基苯磺酸(*p*-TsOH)为催化剂,加入适量的过渡金属化合物(如CF₃SO₃Ag)为助催化剂,在 $p\text{-TsOH}:\text{CF}_3\text{SO}_3\text{Ag}:\text{HCHO}:\text{H}_2\text{O}=100:1:202:202$ (摩尔比), 135 °C, P_{CO} (r.t.) = 10 MPa下反应2 h,乙醇酸甲酯收率可达86.7%,如表4所示,高于同样条件下在有机溶剂中的反应结果.该催化剂体系复杂,离子液体用量大,在重复使用过程中离子液体流动性会降低.

2012年, Song等^[22]报道了功能化酸性离子液体(BAIL)催化甲醛羰基化反应,以三聚甲醛作为甲醛供体,环丁砜为反应溶剂,在 $\text{H}_2\text{O}:\text{HCHO}:\text{BAIL}=10:5:2$ (摩尔比), 170 °C, P_{CO} (r.t.) = 5.0 MPa下反应8 h,乙醇酸甲酯的收率达到了97.6%,结果见表5.催化剂和溶剂重复使用8次,反应活性未见明显下降.酸性离子液体解决了液体酸腐蚀严重、环境污染、不能重复使用等缺陷;克服了固体酸催化剂用量大、活性低、易结焦等问题.他们对酸性离子液体催化甲醛羰基化反应机理进行了推断(图式7).首先,在酸性条件下三聚甲醛解聚生成甲醛;甲醛在离子液体作用下质子化生成羟基碳正离子;后者再与CO反应生成羰基碳正离子;然后和水反应生成乙醇酸.

针对碳一化工发展和聚酯工业原料的需求,依靠我国煤基甲醇资源和技术优势,以甲醛和合成气为原料开展合成乙二醇的研究,以非石油路线新技术补充、代替石油路线制乙二醇的短缺.这项技术的工业化有利于提

高煤和合成气的利用率,优化煤化工产业链,弥补我国聚酯原料的短缺.

3.2. CO偶联法(草酸二酯法)

Unocal公司^[23–25]于1968年提出了CO偶联制备乙二醇的工艺路线(见式(2)),它以廉价的NO, CO, O₂, 醇类和H₂等为反应原料,首先利用醇与N₂O₃反应生成亚硝酸酯,在催化剂PdCl₂-CuCl₂上与CO偶联得到草酸二酯,后者催化加氢制取乙二醇.在125 °C和7.0 MPa下反应,草酸酯的选择性仅为66%.该反应过程实际并不消耗甲醇和亚硝酸酯,只是CO, O₂和H₂参加反应合成乙二醇,反应见式(3).该工艺副产物多,有碳酸二酯, CH₃COOR, CO₂等,乙二醇收率低;反应使用含有卤素的催化剂,设备腐蚀严重;为使反应系统保持无水状态,需要使用大量脱水剂,过程经济性降低.此后, Arco公司和UBE公司^[26]对催化剂体系进行了改进,加入第三组分碱金属盐(LiCl, Na₂CO₃, NaOAc等)、氨或三烷基胺和硫酸盐等,虽不需要使用脱水剂,但设备腐蚀问题仍未能解决.房金刚等^[27]采用K₂CO₃为反应促进剂,乙醇转化率仅为18.0%,草酸二乙酯和碳酸二乙酯的总选择性为79.6%.

1978年,宇部兴产公司和UCC公司通过向反应体系引入亚硝酸酯,解决了Unocal方法腐蚀严重等问题^[28–30].他们采用2% Pd/C催化剂,在亚硝酸酯存在下CO和丁醇偶合,在90 °C和9.8 MPa下反应,草酸酯收率达到了98%.目前,液相反应体系仍存在反应速度慢、副产物多、催化剂流失等缺陷.因此,宇部兴产公司^[31]开发了气相法技术路线,即CO和亚硝酸甲酯或乙酯反应生成草酸二酯,进而气相加氢得到乙二醇,副产物NO与O₂和甲醇反应转化为RONO循环使用.以Pd/Al₂O₃为催化剂,在104~117 °C和0.2 MPa的条件下反应,草酸二甲酯收率可达54.7%.该方法已通过模试,连续运行了480 h,草酸二甲酯平均时空收率为432 g/(L·h),实现了连续催化循环及副产物NO的重复使用;另外,气相法工艺具有选择性高,反应条件温和,不使用溶剂等优点,更具经济优势.

国内从20世纪80年代初期就开始了CO偶联合成草酸酯及其衍生物的研究,所用催化剂多以Pd为活性组分, $\alpha\text{-Al}_2\text{O}_3$ 为载体,但助催化剂有差异,其催化性能见表6.福建物质结构研究所^[32–34]采用20% Pd/ $\alpha\text{-Al}_2\text{O}_3$ 催化剂,在120~175 °C,常压, 3000 h⁻¹条件下反应,草酸二乙酯平均时空收率为750 g/(L·h),并开展了中试研究.华东理工大学赵秀阁等^[35,36]采用Pd-Ce/ $\alpha\text{-Al}_2\text{O}_3$ 为催化剂,CO和亚硝酸甲酯在140 °C进行偶联反应,CO单程转化率为78%,草酸二甲酯时空收率为821 g/(L·h).研究发现增大载体

的比表面积、孔径及孔体积均有利于提高催化剂活性; 助剂有效地提高了Pd的分散度, 并减小了Pd的粒径, CH_3ONO 转化率可以从57.1%提高到84.7%. 天津大学马新宾等^[37–42]制备了Pd-Fe/ Al_2O_3 双金属负载型催化剂(Pd 1.5%, Fe 0.9%), 在110 °C, 0.1 MPa, 停留时间2~3 s下反应, CO单程转化率为32%, 草酸二乙酯时空收率为408~670 g/(L·h). 浙江大学姜玄珍^[43]开发了Pd-Ga/ $\alpha\text{-Al}_2\text{O}_3$ 催化剂体系, CO单程转化率为33%~55%, 草酸二乙酯的选择性为85%. 南开大学郭俊怀等^[44]开发了Pd-Fe-La/ $\delta\text{-Al}_2\text{O}_3$ 多组分催化剂体系, 采用固定床装置, 反应条件为100~130 °C, 停留时间0.5~3 s, 平均收率为3.29 g/(g·h). 华东理工大学赵铁均等^[45]开发的基于纳米碳纤维为载体的CO偶联催化剂, 草酸二甲酯的单程转化率大于85%, 产物选择性接近100%, 为催化剂载体的选择开辟了一条新途径.

陈庚申等^[33]对CO偶联合成草酸酯反应机理进行了深入的研究, 如图式8所示. 他们认为该反应属于亲核反应, 在反应条件下, 活性中心 Pd^0 络合两个CO分子, 形成Pd的羰基配合物, 由于载体和Pd的相互作用, Pd具有较多的负电荷, 羰基上的碳原子带有更多的正电荷, 因此有利于 RO-NO^+ 的 RO^- 亲核进攻. 通过氧化加成反应, 形成双烷氧羰基Pd中间配合物, 活性中心从 Pd^0 转化为 Pd^{2+} , 并放出两个NO分子, 最后该配合物偶联生成草酸酯, Pd^{2+} 又转化为 Pd^0 . 在该反应中, RO-NO^+ 是两分子同时络合在一个活性中心上的二级反应, 这与亚硝酸酯的反应级数是一致的. Meng等^[46]在Pd-Fe/ $\alpha\text{-Al}_2\text{O}_3$ 催化剂上进行了CO偶联生成草酸二乙酯的动力学研究, 认为 EtO-NO 键具有较低的解离能, 容易分裂为 EtO^- 和NO并吸附在活性位点, 两者之间形成平衡. 因此, 反应决速步骤是表面反应. 他们还发现氢气能与 EtO^- 反应生成副产物乙醇.

宋瑛等^[47,48]利用原位红外技术对反应机理进行了研究, 发现CO主要吸附在活性中心Pd上, 并存在线式和桥式两种吸附形式. CO与 Pd^{2+} 的烷氧基配合物反应形成 Pd^{2+} 的双烷氧羰基配合物, 该配合物进一步偶联生成草酸酯, 而 Pd^{2+} 被还原成 Pd^0 . 也就是说, 在CO气相催化偶联合成草酸酯的过程中, 活性组分Pd经历了一个氧化-还原过程(见图式9), 而CO的吸附和转化是该过程决速步骤.

王保伟等^[49]采用XPS实验证实了CO氧化偶联反应按两级“共催化循环”反应模式进行(见图式10). 首先 Pd^0 被亚硝酸乙酯氧化成 Pd^+ 的活性中间体($\text{Pd}^+\text{OC}_2\text{H}_5$); 而Pd的活性中间体继续被亚硝酸乙酯氧化成 Pd^{2+} 的烷基化合物($\text{Pd}^{2+}(\text{OC}_2\text{H}_5)_2$), 吸附在催化剂表面上的线式CO较容易插入到钯(II)烷氧化合物中, 生成双烷氧羰基钯(II)

化合物, 后者在催化剂表面上的空间场(无位阻)足够大时, 可进行还原消去反应, 缔合生成草酸二乙酯. Pd^{2+} 被还原为 Pd^0 时又进入下一次循环. 在整个反应过程中通过与亚硝酸乙酯及CO的反应来改变Pd的价态; 反应过程中催化剂的成分变化和迁移与氧化-还原“共催化循环”机理进行.

林茜等^[50]认为, CO偶联反应发生在桥式CO和气相的亚硝酸甲酯之间, CO的吸附为反应的控制步骤. 由于CO中氧原子的吸电子能力较强, 羰基上的碳原子带有较多的正电荷, 因此有利于 $\text{CH}_3\text{O-NO}^+$ 中 CH_3O^- 基团的亲核进攻, 而 NO^+ 与Pd外层电子作用形成较稳定的线式吸附态NO, 从而生成过渡态的 Pd^{2+} 的双烷氧羰基络合物, 后者偶联脱附形成草酸二甲酯, 具体反应式如式(4).

陈庚申等^[51]报道了在Pd(acac)- PPh_3 催化体系中, CO和亚硝酸酯偶联合成草酸二酯的反应. 在 $\text{PPh}_3/\text{Pd}(\text{acac})_2 = 3$ (摩尔比), 60 °C, $P_{\text{CO}} = 3.0$ MPa下反应, 草酸二乙酯生成率达8.3 mol/(mol·h). 他们发现, 在反应过程中, 催化剂 $\text{Pd}(\text{acac})_2$ 的acac配位体被 PPh_3 取代, 转变为钯苯基膦配合物 $[(\text{PPh}_3)_3\text{Pd}]$, 然后与CO络合生成反应中间配合物苯基膦烷氧羰基钯 $(\text{PPh}_3)_3\text{Pd}(\text{CO})$. 由于CO的配位反应, 其共振价键结构的能量较接近, 容易发生 $\text{Pd-C}(sp) \leftrightarrow \text{Pd-C}(sp^2)$ 变化, 形成类金属烯酮的价键结构的羰基配合物 $[\text{L}_3\text{Pd}=\text{C}=\text{O}]$, 该配合物的羰基碳原子有利于 $\text{RO-N}^+\text{O}$ 上的 RO^- 的亲核进攻, 生成烷氧羰基钯中间络合物, 最后通过两分子的单烷氧羰基钯的还原消除而偶联成草酸酯(见图式11).

目前, CO偶联法生产乙二醇工艺的瓶颈在于草酸二酯催化加氢的工艺还不够成熟. 因而成为很多公司和机构的研究内容, 并开发出了一些催化体系. 20世纪80年代, Matteoli等^[52,53]对贵金属均相催化草酸酯加氢进行了系统的研究和报道, 以钌的羰基配合物 $\text{Ru}(\text{CO})_2(\text{CH}_3\text{COO})_2(\text{P}_n\text{Bu}_3)_2$ 为催化剂, 在180 °C, $P_{\text{H}_2}(\text{r.t.}) = 20.0$ MPa下反应, 乙二醇选择性为82%. 钌系催化剂表现出了优越的催化性能, 但存在价格高、制备难、寿命较短、反应产物和催化剂不易分离等问题, 限制了其工业应用.

1987年, ARCO公司^[54]开发了Cu-Cr催化草酸酯加氢技术, 反应在3.0 MPa的压力下进行, 乙二醇收率为95%, 但由于Cr对生态环境破坏严重, 且不易回收, 开发前景不容乐观. UCC公司以Cu/ SiO_2 为催化剂, 在180~240 °C, 3.0 MPa, 氢酯比为67(摩尔比)的条件下反应, 草酸二甲酯的转化率近100%, 乙二醇的选择性为97%. 1994年, Engel-

hard公司^[55]报道了Cu-Zn的氧化物和少量Al₂O₃催化剂体系,也取得了不错的效果。

国内对草酸酯加氢制乙二醇的研究以气相法为主,催化剂性能见表7。福建物构所^[56]采用负载型Cu-Cr/SiO₂催化剂,在205~240 °C, 2.5~3.0 MPa, 氢酯比60(摩尔比)的条件下反应,草酸二乙酯转化率达到99.8%,乙二醇选择性为95.3%。天津大学^[57]采用Cu-Zn/SiO₂催化剂,在200~250 °C, 3.0 MPa, 氢酯比为30~100(摩尔比)的条件下,草酸二乙酯转化率为95%,乙二醇收率在80%左右。华东理工大学李竹霞等^[58,59]研究了Cu/SiO₂催化剂体系,在205 °C, 2.5 MPa, 氢酯比为80(摩尔比)下反应,乙二醇收率达到了99.1%。

CO偶联工艺原料复杂,采用贵金属催化剂,成本高,工艺流程长,副产物水易与氮氧化物反应生成硝酸,造成设备腐蚀。目前,加氢技术一直未取得突破。

3.3. 甲醛氢甲酰化法

Monsanto公司于20世纪80年代初开发了甲醛氢甲酰化反应制备乙二醇技术,即甲醛首先与合成气反应得到乙醇醛,后者加氢生成乙二醇(见式(5))。由于钴对于C-C键插入能力较弱,反应活性和选择性都较低,研究主要集中在铑系催化剂上。最初,采用羰基铑催化剂,产物收率在50%以下,反应速率低^[60]。

Monsanto公司^[61]发现在Rh催化的甲酰化反应中,以二取代胺类化合物为溶剂时有利于甲酰化反应,副产物甲醇选择性明显降低。研究者认为主要是由于溶剂的电子效应。Goetz等^[62]进一步对反应溶剂进行了考察,发现以苄腈为溶剂时反应活性较高。此后,Halcon公司^[63]在铑催化剂体系中加入膦酰胺配体PPh₂CH₂CH₂C(O)N(CH₃)(C₁₈H₃₇),在乙腈/醚溶剂中反应,进一步提高了乙二醇的收率。

Chan等^[64]研究发现,采用过量的膦配体作为稳定剂,有利于提高催化剂的稳定性,但是削弱了Rh的催化活性;然而加入少量的胺或烷基吡啶作为促进剂,可显著提高羟基乙醛的选择性。在此基础上,Okano等^[65]以RhCl(CO)(PPh₃)为催化剂,以4-甲基吡啶为溶剂,在70 °C反应4 h,羟基乙醛的收率超过90%。在反应体系中引入质子酸,反应转化率提高至99.8%,羟基乙醛的选择性为95%,主要副产物为甲醇(仅为1.9%)。

1987年, Marchionna等^[66]以Rh₄(CO)₁₂为催化剂,在丙酮溶剂中考察了助剂卤化物Bu₄NX对反应的影响,发现Bu₄NX具有良好的助催化作用,主要是由于氯化物在反应体系中具有良好的溶解性,形成卤化物络合离子

[Rh(CO)₂X₂]⁻, [Rh₅(CO)₁₅]⁻和[Rh₅(CO)₁₄X]²⁻参与了甲醛活化(式(6)), 卤素的助催化活性顺序为Cl>I>Br>F(见表8)。以多聚甲醛为甲醛供体,在110 °C, 13.7 MPa下反应2 h, 甲醛转化率可达77.8%, 羟基乙醛选择性为74.6%。随后,他们^[67]报道了复合催化剂[Rh(CO)₂Cl₂]⁻和[Rh₅(CO)_{15-x}(PPh₃)_x]⁻催化甲醛氢甲酰化反应活性,采用多聚甲醛作为甲醛供体,丙酮为反应溶剂,在110 °C, 9.6~14.2 MPa (CO:H₂=1)下反应,产物选择性达到了95%。

1995年, Ezhova等^[68]研究了RhCl(PPh₃)₃, RhCl(CO)(PPh₃)₂和RhCl₃+PPh₃催化甲醛氢甲酰化反应,在*N,N*-二甲基乙酰胺体系中, RhCl₃+PPh₃表现出了优越的催化活性,在T≤110 °C, P_{CO+H₂}≥12 MPa, [H₂O]≤1.8 mol/L, [Rh]≤2.5×10⁻³ g/L, [CH₂O]≤0.03 g/L下反应,反应物转化率为62%~67%,羟基乙醛选择性为96%。在Rh配位作用下,羟基乙醛和甲醛缩合生成C₃~C₁₆的多羟基醛,以及乙醇醛的二聚体。随后Ezhova等^[69]以RhCl(PPh₃)₃为催化剂,采用原位红外光谱对催化机理进行了考察(式(7)), RhCl(PPh₃)₃首先和CO反应生成单羰基化合物RhCl(CO)(PPh₃)₂,继而二羰基化合物RhCl(CO)₂(PPh₃)₂,随后脱去HCl形成羰基氢化物RhH(CO)₂(PPh₃)₂,在溶剂*N,N*-二甲基甲酰胺中脱去一个质子形成催化活性中间体[Rh(CO)₂(PPh₃)_x(DMAA)_y]⁻ (x=1, 2; y=1, 0)和[Rh(CO)₄]⁻。Ezhova等^[70]进一步研究发现,催化剂前体RhH(CO)(PPh₃)₃, RhCl(CO)(PPh₃)₂, RhCl(PPh₃)₃, RhCl(CO)(PPh₃)₂和[RhCl(CO)₂]₂等在氢甲酰化反应过程中均形成了阴离子复合物[Rh(CO)₂L_x(DMAA)_y]⁻ (L=PPh₃, PPh₃; x=1, 2; y=1, 0)和[Rh(CO)₄]⁻,作为催化活性中间体参与甲醛活化。

Costa^[71]对HM(CO)_n催化甲醛氢甲酰化反应机理进行了推断(见图式12)。甲醛首先与催化剂络合生成反应中间体HOCH₂C(O)M(CO)_{n-1},而HOCH₂C(O)M(CO)_{n-1}在反应条件下解析出羟基乙醛,进一步加氢得到乙二醇。

氢甲酰化法只有采用三聚甲醛或多聚甲醛作为甲醛供体时才表现出较高的转化率,原料成本高,反应过程中甲醛易发生还原反应生成甲醇,并与之形成的聚糖缩合。催化剂多采用Rh配合物,成本较高。为此,开发催化剂的重复使用,寻求高活性的非铑催化剂体系尤为重要。

3.4. 甲醛缩合法

除此之外,间接法合成乙二醇的路线还有:甲醛缩合法和甲醛电化加氢二聚法等,目前大都停留于小试阶段。

Weiss等^[8]以30%的甲醛水溶液为反应原料,在NaOH溶液中经沸石催化合成羟基乙醛,然后在94 °C,常压,空速 1.21 h^{-1} 和Ni催化剂下,加氢还原为乙二醇(式(8)).羟基乙醛收率为75%.目前加氢技术研究进展缓慢.

Sanderson等^[72–74]以 $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$ 为引发剂,在1,3-二氧杂烷存在下,将甲醛加氢缩合生成乙二醇,同时生成甲酸甲酯,反应循环见式(9).乙二醇选择性随着反应温度的降低而升高,在75 °C下反应,乙二醇选择性为44.9%.

1984年,Associate^[75,76]开发了甲醛电化加氢二聚制乙二醇技术,以甲醛水溶液为原料,甲酸钠为电解质载体,加入甲酸维持电解液的pH为4.4. 1991年,Weinberg等^[77]以39.5%的甲醛水溶液为反应原料,采用石墨电极(Ultracarbon ST-50),电解液pH值控制在5.5~6.5,在80~90 °C下反应,有效地抑制了副反应的发生,乙二醇选择性和收率约为90%,在最优反应条件下甚至达到了99%.该工艺反应条件温和,但耗电量大、产物浓度低.

4. 结语

在当前国际油价居高不下,我国原油资源短缺,煤资

源相对丰富的情况下,大力开展建立在煤炭资源基础上碳一化工的基础及应用研究极为重要,尤其在国家能源安全、产业结构多元化方面,实现煤气、发电、化工一体化的高效能源化工系统,可形成煤炭工业发展新模式.以煤和合成气为原料制备乙二醇技术对发挥煤炭资源优势,推动煤化工产业的发展,弥补我国油气资源的不足和聚酯原料的短缺,保障能源安全,促进经济的可持续发展具有重要意义.

合成气直接制备乙二醇的反应条件过于苛刻,但具有原子经济性,如有突破将非常有竞争力,但目前的成果还不足以工业化.甲醛羰基化法原料来源丰富,成本低,现已开发了环境友好、可循环使用的离子液体催化剂体系,克服了传统液体酸分离困难、设备腐蚀严重等缺陷,具有较好的研究开发前景.CO偶联法在我国已有中试装置,反应条件相对温和,但原料复杂,采用贵金属催化剂、成本高,工艺流程长,副产物水易与氮氧化物反应生成硝酸,造成设备腐蚀.甲醛氢甲酰化法以三聚甲醛或多聚甲醛为甲醛供体,以贵金属铑为催化剂,成本较高.甲醛缩合法具有反应条件温和、选择性和收率高等优点,也很有吸引力.