



Study on a New Catalyst Tungsten Phosphide for the Carbon Dioxide Reforming of Methane and Its Preparation Conditions

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(Received: 29 February 2012;

Accepted: 7 January 2013)

AJC-12657

A new tungsten phosphide was successfully synthesized for the carbon dioxide reforming of methane (CH₄-CO₂ reforming). The catalysts were prepared by combining citric acid and temperature programmed reduction of phosphotungstate precursor, which was characterized by X-ray diffraction. This paper focuses on investigating that the influence of preparations on activity of tungsten phosphide for CH₄-CO₂ reforming. The activity results indicate that the activity and stability of catalyst was prepared under the proper conditions. On this basis, a new easier preparation was proposed, which was prepared by associating calcining with reduction H₃O₄₀PW₁₂·XH₂O and (NH₄)₂HPO₄, the prepared catalyst showed a little bit worse of the activity. The activity test results of tungsten phosphide for CH₄-CO₂ reforming show that it produce synthesis gas with lower H₂ to CO ratio than the conventional catalysis for the CH₄-CO₂ reforming.

Key Words: WP Catalyst, CH₄-CO₂ reforming, Preparation, Phosphotungstate.

INTRODUCTION

Natural gas (the main ingredient is CH₄) which is increased in the proportion of energy structure of the world year by year. All of the major greenhouse gases have also increased in recent years, especially CH₄ and CO₂. Therefore, it is significant to do research on their utilization. The reforming of methane with carbon dioxide for the production of synthesis gas (CO + H₂) is appealing because it produces synthesis gas with higher purity and lower H₂-to-CO ratio than either partial oxidation or steam reforming¹. This low ratio of synthesis gas is suitable for the methanol, ammonia and Fischer-Tropsch. On the environmental and energy perspective, both CH₄ and CO₂ production and utilization could effectively alleviate energy crisis and themselves emission. Thus the CH₄-CO₂ reforming is very important².

To select the appropriate catalyst is one of the key factors, which catalyst should to activate and directionally transform small molecular CH₄ and CO₂. Most of the group VIII elements are known as being activity for CH₄-CO₂ reforming, according to Hirose *et al.*³. The activity order of non-precious metals is Ni > Co > Cu > Fe⁴. However, the non-precious metals inactivated rapidly during the reforming due to carbon deposition (such as nickel⁵). Although, the noble metals exhibit not only the characteristics of high transforming activity, but also higher resistance to carbon deposition, whereas they cost too much.

In recent years, scholars have conducted a lot of work to find a suitable way of industrialization in this area, so the issue was deeply studied. Thus, their efforts have been concentrated on how to reduce carbon formation and exploring new non-precious metal catalysts, which have resistance to carbon deposition, high activity and good stability. Li *et al.*⁶ have attracted many attentions because of the high activity and good stability of a new molybdenum phosphide (MoP) catalyst for CH₄-CO₂ reforming, which prepared by readily available materials and a simple craft. Tungsten and molybdenum with similar chemical and physical properties based on the chromium group and valence electron structure. This report shows how to prepare tungsten phosphide (WP) catalyst by similar methods and measured catalytic activity of CH₄-CO₂ reforming, the result showed that the reaction with the as-prepared tungsten phosphide catalyst was stable and efficient.

EXPERIMENTAL

Preparation tungsten phosphide (I): The tungsten phosphide catalyst was successfully synthesized by using the analytically pure (NH₄)₅H₅[H₂(WO₄)₆]·H₂O as tungsten source, (NH₄)₂HPO₄ as phosphorus resource, citric acid (CA) as chelator^{7,8}. Weighed reactant by molar ratio of W/P/CA = 1:1:1 were dissolved in 30-40 mL of distilled water. Subsequently the solution was aged in a covered beaker in a water bath at 363 K for 12 h. After a further drying at 393 K overnight, the

TABLE-1
PREPARED WP CATALYSTS IN DIFFERENT CONDITIONS

Prepared condition	Catalysts							
	A ₆	A ₈	A ₁₀	A	A ₁₄	A ₁₈	A ₂₄	B
Aged time (h)	6	8	10	12	14	18	24	12
Environmental	Autoclave					Constant temperature bath		
Reactant ratio	n(W:P:CA) = 1:1:1					n(W:P:CA) = 1:1:1		

sample was calcined at 773 K for 5 h in a fluid air and then cooled to room temperature naturally to get the precursor. Some products were taken into U-tube and then reduced by temperature programmed (followed: from room temperature to 573 K in 0.5 h, after from 573-923 K at a heating rate of 1 K/min and then kept at 923 K for 2 h) in a stream of H₂ (purity as 99.999 %, velocity as 60 mL/min). Finally, the surface of samples was passivated in a flow of 0.5 % O₂/He for 12 h.

The prepared tungsten phosphide catalyst was marked as A by above-mentioned method. The tungsten phosphide catalysts were prepared by difference aged time in a covered beaker and they were labeled as: A₆, A₈, A₁₀, A₁₄, A₁₈, A₂₄, the number in labels show that the aged time of tungsten phosphide catalysts. The reactive solution was stirred in 363 K thermostatic water bath for 12 h instead of autoclave that was mentioned, the prepared tungsten phosphide catalyst was denoted hereafter as B. These catalysts are shown in Table-1.

Preparation of tungsten phosphide (II): A certain amount of phosphotungstic acid H₃O₄₀PW₁₂XH₂O (PWA) directly calcined in a muffle furnace at 773 K for 5 h in air and then cooled to room temperature naturally, then the samples were reduced and passivated in the same way. The prepared tungsten phosphide catalyst was marked as C.

A certain of PWA and (NH₄)₂HPO₄, the molar ratio was adjusted to W:P = 1:1, subsequently, the steps were the same as catalyst C. The formed tungsten phosphide catalyst was denoted as D. The catalysts are shown in Table-2.

TABLE-2
TWO DIFFERENT CATALYSTS

Prepared conditions	Catalyst	
	C	D
Reactant ratio	PWA	PWA and (NH ₄) ₂ HPO ₄ n(W:P) = 1:1
Pretreatment before calcination	Unmiling	Miling

Activity test of catalysts: The amount of catalyst was 150 mg, which was taken into U-tube for testing activity of CH₄-CO₂ reforming in a fixed bed reactor. Before each test, the catalyst was purged with N₂ (30 mL/min) at 873 K for 10 min, then reduced in H₂ (99.999 %, 60 mL/min) at 923 K for 2 h. Finally, the activity tests were carried out at 973, 1023 and 1073 K with the analytical system (GC 102 M gas-chromatograph, thermal conductivity detector TCD), which reactants were mixture of CO₂ and CH₄ (the molar ratio nCH₄/CO₂ = 1:1) with space velocity of 12000 mL/(h g cat). At the same time, the carrier gas was helium, which velocity as 30 mL/min.

Stability testing of catalysts: The amount of catalyst also was 150 mg. Catalytic stability tests were carried out at 1023 K in a flow microreactor directly with the analytical system.

The CH₄-CO₂ mixture and other conditions of gas-chromatograph were the same as the activity test of catalyst, but the space velocity of mixture adjusted to 6000 mL/(h g cat). The catalysts were also pre-treated in flowing H₂ at 923 K for 2 h.

X-Ray diffraction: Patterns of the intermediates as well as the final samples were determined with a Rigaku diffractometer operated at 40 kV and 100 mA, using CuK_α monochromatized radiation (λ = 1.5432 Å).

RESULTS AND DISCUSSION

Influence of aged time: Catalysts of A₆, A₈, A₁₀, A, A₁₄, A₁₈ and A₂₄ were tested activity for CH₄-CO₂ reforming at different temperature, the results are summarized in Table-3.

TABLE-3
DIFFERENT CATALYSTS TESTED ACTIVITY FOR CH₄/CO₂ REFORMING AT DIFFERENT TEMPERATURES

Catalyst	Conversion (%)					
	973 K		1023 K		1073 K	
	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
A ₆	40.3	94.8	63.2	97.6	76.1	98.3
A ₈	44.4	94.6	64.7	96.7	88.8	1.0
A ₁₀	42.9	93.3	44.5	95.2	54.6	96.1
A	43.8	99.5	55.0	98.2	70.0	96.8
A ₁₄	38.2	78.4	40.3	91.5	43.1	95.7
A ₁₈	46.5	88.5	60.6	91.6	81.5	94.8
A ₂₄	33.2	80.8	43.1	82.3	49.9	90.1

Table-3 shows that the catalytic activity of A₈ the same as A₁₈ at different experimental temperature, but better than other five kinds of catalysts. The phenomenon suggests that aged time has some effect on the catalytic activity. If the catalysts of weak activity were prepared, maybe the reactants were not responded at all in the short aged time. If the aged time was too long, maybe the prepared catalysts had weak activity at higher temperature due to poor antisintering.

Table-3 also shows that their activity increased in varying degrees with the raising of aged temperature. The catalytic activity can be improve by the endothermic reaction of CH₄-CO₂ reforming on the one hand (temperature ascending is favour of thermodynamic equilibrium) and the number of active center is increasing as the surface of tungsten phosphide precursors, which is reduced gradually to tungsten phosphide on the other hand. But, higher temperature would cause high energy consumption.

Stability of A₈ and A₁₈: The tungsten phosphide catalysts were prepared by different aged time in a covered beaker. The catalyst of A₈ and A₁₈ were measured the stability for 12 h. The results are shown in Fig. 1, in which the A₁₈ catalyst showed a better stability. The A₈ catalyst was no longer to be tested because of its low activity after 5 h test. A₈ catalyst was not stable due to lack of aged time and the aged was inadequate.

TABLE-4
ACTIVITY OF A AND B CATALYSTS IN DIFFERENT ENVIRONMENT

Reaction temperature T (K)	Sample	Conversion (%)		Composition of products and reactants (%)			
		CH ₄	CO ₂	CH ₄	CO ₂	CO	H ₂
927	A	38.4	99.5	33.1	0.2	49.2	17.6
	B	41.2	97.4	31.5	1.2	45.9	21.4
1023	A	55.0	98.2	24.1	0.8	46.1	29.0
	B	56.6	98.0	23.3	0.9	43.5	32.3
1093	A	70.1	96.8	16.1	1.5	46.9	35.5
	B	78.6	99.1	11.5	0.4	46.5	41.6

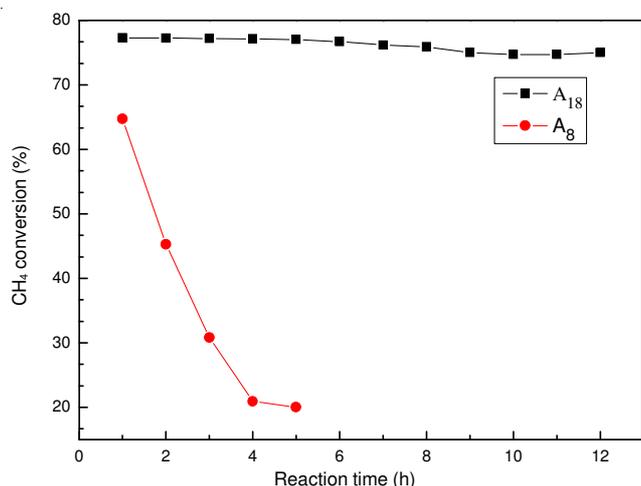


Fig. 1. Stability tests of A₈ and A₁₈ catalysts

Influence of aged environment: The performance of the catalysts (A and B) was measured in CH₄-CO₂ reforming at different temperatures. The results are shown in Table-4. Table-4 shows that the activity of catalyst B are better than A at different experimental temperatures. It maybe due to the aged was more fully in 363 K constant temperature water bath and stirring than in the autoclave.

Influence of preparation methods: The performance of the catalysts (C and D) in CH₄-CO₂ reforming was tested at different temperatures. The test results were compared with the catalytic activity of A₁₈ (Table-5). Table-4 showed that the catalytic activity was related to proportion of P element in tungsten phosphide and the catalyst has good activity when the molar ratio of W:P = 1:1 from the current experimental tests (such as D and A₁₈ catalyst). The activity of D catalyst is similar to that of A₁₈. However, preparation of D catalyst was easier than A₁₈. This is a suitable way of industrialization.

TABLE-5
ACTIVITY OF A₁₈, C AND D CATALYSTS
PREPARED BY DIFFERENT METHODS

Reaction temp. T (K)	Sample	Conversion (%)		Composition of products and reactants (%)			
		CH ₄	CO ₂	CH ₄	CO ₂	CO	H ₂
973	A18	46.5	88.5	27.6	5.4	45.2	21.8
	C	44.9	78.8	29.5	9.8	42.5	18.2
	D	45.3	99.1	29.3	0.4	47.1	23.1
1023	A18	60.6	91.6	21.2	3.9	44.2	30.7
	C	57.1	96.6	23.0	1.6	41.2	34.2
	D	65.9	97.1	18.3	1.4	46.0	34.3
1073	A18	81.5	94.8	9.9	2.4	45.7	42.0
	C	70.7	95.1	15.7	2.3	42.4	39.6
	D	76.1	96.0	12.8	1.9	47.9	37.4

Specially, the synthesis gas produced by these catalysts had lower H₂ to CO ratio than the conventional catalysts for the CH₄-CO₂ reforming did, which was detected from Tables 3-5. The reason was that could be caused by the process (CO₂ + H₂ → CO + H₂O) and the side reaction more likely occurred by the WP catalyst.

X-ray powder diffraction analysis: The prepared products (A₁₈, C and D) were characterized by powder X-ray diffraction (Fig. 2). As expected, the catalysts A₁₈ and D have characteristic diffraction peaks of tungsten phosphide (PDF29-1364) crystalline phase, which were measured 2θ degree for 21.1, 28.7, 31.1, 43.2, 44.6, 46.5, 68.8 and 73.8° end so on, respectively. However, the patterns of D catalyst shows that its crystal was formed weakly because of lower calcined temperature and there was the tungsten phosphide oxide (WOPO₄) (PDF44-0348) diffraction peaks also detected from this pattern and the 2θ degree for 15.9, 21.7, 23.1, 33.2, 36.4, 40.5, 49.6 and 55.3° etc., respectively. The reason was that may be the nanophases WOPO₄ formed in the calcination stage of the reactants and did not reduce at the TPR of phosphotungstate precursor stage. So the activity of A₁₈ catalyst was better than that of D catalyst. Obviously, the C catalyst have characteristic diffraction peaks of W (PDF47-1319) and the 2θ degree for 35.5, 39.9, 43.9, 63.8, 66.7, 69.6, 86.0 and 88.7° etc., respectively. The reason is that the C catalyst was prepared directly by the PWA. Obviously, the molar ratio of P/W was 1:12 from chemical formula of the H₃O₄₀PW₁₂·XH₂O and the content of W element is higher than tungsten phosphide in the product after reduction. So there were no evidently tungsten phosphide different peaks detected, except the 2θ degree for 49.9, 63.9, 73.8 and 85.8°. The appearance of WO₃ diffraction peaks (PDF46-1096) because of the C catalyst exposed to the air resulting in the partially oxidized of the surface. Thus, the catalytic activity of D catalyst is higher than that of C catalyst for the CH₄-CO₂ reforming. This is consistent with the experimental results. Reported in the literature, the W element for CO₂ reforming of CH₄ has no activity⁹.

Conclusion

The tungsten phosphide with activity in CH₄-CO₂ reforming was successfully prepared by temperature programmed reduction of amorphous phosphotungstate. In the view of current experiment, the tungsten phosphide with good activity and stability was prepared by stirring for 18 h in 363 K thermostatic water bath and also can obtain directly by calcining and reduction of the H₃O₄₀PW₁₂·XH₂O and di-ammonium hydrogen phosphate. The activity test results of tungsten phosphide for CH₄-CO₂ reforming show that it products synthesis gas produced by this method had lower H₂ to CO ratio than the conventional catalysts for the CH₄-CO₂ reforming did, which could be caused by the process (CO₂ + H₂ → CO + H₂O).

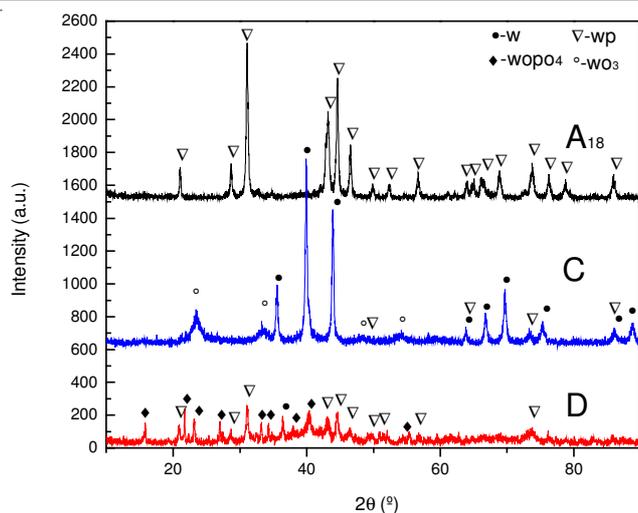


Fig. 2. Powder XRD patterns of A₁₈, C and D

ACKNOWLEDGEMENTS

This work was supported by a grant from the National Natural Science Foundation of China (21063010).

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