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# CATALYTIC PROPERTIES OF SUPPORTED MO<sub>2</sub>C SYNTHESIZED BY MICROWAVE IRRADIATION IN HYDRAZINE HYDRATE DECOMPOSITION REACTION

#### A. M. AGHOYAN, R. A. MNATSAKANYAN and D. H. DAVTYAN

 A.B. Nalbandyan Institute of Chemical Physics NAS RA 5/2, P. Sevak Str., Yerevan, 0014, Armenia E-mail: artur.aghoyan@gmail.com

Microwave-assisted synthesis and catalytic processes of Mo<sub>2</sub>C/carrier systems have been studied. Catalytic tests were carried out on hydrous hydrazine decomposition reaction. Supported Mo<sub>2</sub>C has shown catalytic activity in decomposition reaction. The catalytic activity changes depending on the carrier's characteristics. The highest catalytic activity is observed in the reaction with Mo<sub>2</sub>C/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system (95.4%). In all cases decomposition of hydrazine was 100% selective with respect to ammonia and nitrogen.

Figs. 2, table 1, references 18.

## Introduction

It is known that transition metal carbides show high catalytic activity in a number of reactions. For practical purposes, the catalysts are used in combination with different carriers, giving them different properties. As an example, alumina-supported molybdenum carbide ( $Mo_2C$ ) was tested as a catalyst for hydrazine decomposition in a monopropellant thruster [1]. Also known the high catalytic activity of microwave-synthesized tungsten carbide-carbon (WC-C) system in hydrazine hydrate ( $N_2H_4$ ·H<sub>2</sub>O) decomposition [2]. The above mentioned metal carbides, in particular molybdenum carbide, were synthesized by various methods such as temperature-programmed reduction of molybdenum oxide [3], plasma-assisted synthesis [4], solution combustion synthesis [5], microwave-assisted synthesis [6].

The present work includes the study of the synthesis and catalytic properties of  $Mo_2C$  in a microwave oven in combination with different carriers. For the studies hydrazine hydrate decomposition was chosen as a model reaction.

In today's modern chemical industry, time is the most important and expensive capital. This quote is certainly also true for Science. Particularly a lot of experimental research is being done to develop, optimize and find new synthetic routes, which is a time-consuming process. From this point of view, any new synthesis method that will save time is extremely important to science as it allows more experiments to be done simultaneously to achieve the desired result. Microwave chemistry seems to meet this requirement and is an indispensable rapid synthesis tool in modern synthesis [7, 8, 9]. In the last decades, microwave chemistry has evolved significantly in different directions. Such areas are organic [10] and inorganic chemistry, in particular new and more effective synthesis of materials, analytical chemistry, biochemistry, catalysis and photochemical processes that have achieved great success in applying microwave irradiation as a source of heat [11].

Since the 1990s, there has been great interest in conducting heterogeneous catalytic reactions under the influence of microwave irradiation (MW) [12]. The results of research show that such speeds of chemical reactions cannot be achieved at conventional heating under the same conditions and time periods, which are possible in microwave ovens. The unique interaction between the catalyst and the microwave irradiation appears to be a means of speeding up the intermediate chemical reaction, which leads to similar results.

Microwave irradiation is electromagnetic radiation in the frequency range 0.3 to 300 GHz, which corresponds to wavelengths of 1 mm to 1 m. The frequency used in domestic microwave ovens is 2.45 GHz with a wavelength of 12.25 cm, which is used for the study of catalytic chemical reactions. Considering the recent experience, the following advantages and features of microwave heating can be distinguished: rapid heating and cooling of the system (homogeneous heating), obtaining of nanoparticles with relatively narrow particle size distribution and extremely short time of processes which bring to huge energy savings. Given the well-known fact that semiconductors (they are often heterogeneous catalysts, transition metal carbides, borides) are good microwave absorbers [13], there is a need to conduct heterogeneous catalytic processes under microwave irradiation. As was mentioned above, in the present work have been investigated the catalytic properties of microwavesynthesized Mo<sub>2</sub>C (in the presence of different carriers) in the reaction of hydrazine hydrate decomposition. The choice of the hydrazine decomposition reaction is due to its high applicability. Depending on the direction of the hydrazine decomposition reaction, it is used for different purposes. Specifically, when the catalytic decomposition of hydrazine is accompanied by a large amount of heat dissipation (reaction I), it is used as monopropellant for satellite propulsion [14, 15]. Selective catalytic degradation of hydrazine hydrate leads to large amounts of pure hydrogen depletion for fuel cell (reaction II) [16]. In recent decades there have been numerous studies on the decomposition of hydrazine hydrate using different catalysts.

$$3N_2H_4 = 4NH_3 + N_2 (I)$$
  
 $N_2H_4 = N_2 + 2H_2 (II)$ 

Although transition metal series carbides as catalysts have been extensively studied, there are few works in which carbides have been synthesized with a combination of carriers that may affect the carbide catalytic properties. The current work is dedicated to the study of the catalytic activity of microwave-assisted synthesized Mo<sub>2</sub>C in the presence of different acidic carriers on the hydrazine hydrate decomposition reaction.

## Materials and methods

Microwave-assisted synthesis of  $Mo_2C$ ,  $Mo_2C/C$ ,  $Mo_2C/ZSM12$  and  $Mo_2C/\gamma - Al_2O_3$ .

The following materials were used to obtain molybdenum carbide in combination with different carriers: MoO<sub>3</sub> (high purity), carbon (VulcanXC-72R, Cabote corp. 250  $m^2/g$ ), zeolite (ZSM 12, 280  $m^2/g$ , SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> – 25) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Rhone-poulene, 200  $m^2/g$ ).

Microwave synthesis of molybdenum carbide is well known in the literature [6]. In this study, carbide / carrier system synthesis was performed in a similar manner in the microwave oven.  $MoO_3$  and carbon in stoichiometric ratio were taken to obtain pure carbide ( $Mo_2C$ ).

$$2MoO_3 + 7C = Mo_2C + 6 CO \{g\}$$

To obtain  $Mo_2C/C$ , in initial mixture carbon was taken in excess, according to the following reaction:

$$2MoO_3 + 11C = Mo_2C / C + 6 CO \{g\}$$

For the synthesis of Mo<sub>2</sub>C/ZSM12 and Mo<sub>2</sub>C/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> systems, MoO<sub>3</sub> / zeolite (ZSM12)/C and MoO<sub>3</sub>  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> / C were taken respectively. In all the mentioned systems the mass ratio of raw materials were calculated so that the mass fraction of the catalyst (Mo<sub>2</sub>C) in the finished material was 70 wt.% [6]. Microwave-assisted synthesis of supported molybdenum carbide was performed in a quartz tube reactor in a nitrogen flow. The precursor was placed in the reactor, which was then purged with nitrogen for 2 *h* at room temperature. Domestic microwave oven (Electrolux EMS 2820) with a frequency of 2.45 *GHz* and 900 *W* was used to irradiate the tube for up to 600 *s* [6].

The crystal structure and phase composition of the products were determined by X-ray diffraction (XRD) analysis with Ni-filtered CuK $\alpha$  radiation 1, 54018 A<sup>0</sup> (D8 Advance, Bruker) operated at 40 kV and 40 mA. The average diameter of molybdenum carbide crystals was determined by the Scherer's method, from which the specific surface areas were evaluated. Since the adsorption method is not known for separately estimating the specific surfaces

of molybdenum carbides and carriers, the estimation was performed in the manner described above.

Synthesis temperature was measured from a window opened in the back of the microwave oven using an infrared pyrometer (Dostmann electronic GmbH HT 1800). Measurements showed that in all cases the temperature of the synthesis was 1050-1150°C.

## **Catalytic experiments**

The catalytic activity of supported Mo<sub>2</sub>C was tested. For that 0.3 g of catalysts was taken and placed in a Teflon-lined autoclave with a volume of 65  $cm^3$  then 5 ml of diluted hydrous hydrazine 1% solution was poured. The closed autoclave was inserted in a microwave oven and irradiation was carried out at 180 W for 180 *sec*. After the test, the autoclave was removed from the oven, the catalyst was separated by filtration, and the hydrazine concentration was determined by iodometric titration method according to GOST 19503-88 [17]. Separately the catalytic activities of the carriers were tested. For the test 0.09 g (as the mass fraction of carriers in the outgoing catalyst mass 30% wt.) of carriers – C,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and zeolite ZSM 12 and 5 *ml* of 1% hydrous hydrazine solution were taken. It has been shown that the selectivity of hydrazine decomposition is 100% in relation to ammonia and nitrogen formation [6].

## **Results and discussion**

Figure 1 shows the XRD patterns of the final product  $Mo_2C$  (fig.1). As it is seen within the sensitivity range of X-ray analysis, the conversion of initial mixture is 100%. The crystals of molybdenum carbide calculated from the XRD patterns with Scherrer's formula, have nano sizes (Table). The specific surface area of  $Mo_2C$  in  $Mo_2C$ /carrier ( $Mo_2C$ ,  $Mo_2C/C$ ,  $Mo_2C/ZSM12$  and  $Mo_2C/\gamma$ - $Al_2O_3$ ) systems from the calculated crystal sizes was also estimated (Table).



Fig. 1. XRD diffractogram of synthesized molybdenum carbide.

In Figure 2 the XRD patterns of the initial ZSM 12 and synthesized final product are presented. The precursor zeolite is characterized by  $2\Theta = 7$  and  $9^{0}$  angles (Fig. 2a) [18]. After the synthesis, the XRD characteristic lines of the zeolites have disappeared, suggesting that the outgoing zeolite was subjected to phase conversion at high temperatures (Fig. 2b).



Fig. 2. XRD diffractograms of initial ZSM 12 a), and synthesized final product b).

In previous works it has been shown that the  $Mo_2C/C$  system has significantly high catalytic activity during hydrazine hydrate decomposition under the influence of MW [6]. Given this, an attempt has been made to combine different carriers with molybdenum carbide to increase its catalytic activity. For this purpose, carriers with different physicochemical properties, from weakly acidic to strong acidic properties, have been selected for the synthesis. Studies have shown that the percentage of hydrazine conversion depends on the carrier used. In our case, molybdenum carbide catalytic activity on different carriers can be presented in the following order:

$$Mo_2C/Al_2O_3 > Mo_2C/C > Mo_2C > Mo_2C / ZSM - 12$$

Since hydrazine is a basic molecule by its nature, it can be assumed that the first step of its interaction with the catalyst will be with the acid sites, which in some cases may be the limiting step (reaction 3)

$$N_2H_4 + S = N_2H_4 \cdot S$$
 (3),

where S is the surface acidic site. This site can be both on the surface of the carbide and on the carrier. The carriers have almost no catalytic activity (Table) therefore the catalytic decomposition of hydrazine has been attributed to molybdenum carbide. The highest conversion rate was observed during the  $Mo_2C/\gamma$ -Al<sub>2</sub>O<sub>3</sub>+N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O reaction (Table). It is assumed that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, having a pronounced acidic property, provides a high concentration of basic hydrazine at the catalyst surface, which in turn provides good microwave absorption at an appropriate temperature, which results in such a high yield (95% approx.).

Although literature acknowledges that zeolite systems have strong surface acidity, but in our case the  $Mo_2C/ZSM$  12 +  $N_2H_4$ · $H_2O$  reaction shows the lowest conversion rate (Table ). It is known that the degradation temperature of low SiO<sub>2</sub> containing ZSM 12 zeolites is about 700°C [18]. It is assumed that during the carbide synthesis, as already mentioned, degradation of the zeolite results in a loss of acidity.

The catalytic activity of individual carriers without the presence of a catalyst has also been studied. It is found that the carriers  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and zeolite ZSM 12 show absolute catalytic inertia (Table). However, carbon shows some minor catalytic activity (approx. 8%, Table) which is explained by the formation of active centers on the surface of the carbon when it interacts with microwave irradiation.

As has been shown in the previous work [6], Mo<sub>2</sub>C, Mo<sub>2</sub>C/C has catalytic activity due to the presence of surface acid centers. However, our research has shown that the carriers have a large share in the catalytic process, which results in 100% selectivity.

Table

Sample	Conv.,	d <sub>Mo2C</sub> , nm	S, $m^2/g$ of	Conv., $\%/m^2$
	%	2	Mo <sub>2</sub> C	Mo <sub>2</sub> C
70%Mo <sub>2</sub> C /ZSM -12	41	23	28.4	1.44
70%Mo <sub>2</sub> C/C	61.15	28	23.3	2.62
70%Mo <sub>2</sub> C/Al <sub>2</sub> O <sub>3</sub>	95.4	21	31.1	3.07
Mo <sub>2</sub> C	52.5	30	21.8	2.41
С	8.03	_	_	_
Al <sub>2</sub> O <sub>3</sub>	0	—	—	-
ZSM -12	0	_	_	-

## Conclusions

Microwave irradiation allows to synthesize Nano scale carrier-supported Mo<sub>2</sub>C, which shows high selective catalytic activity in hydrous hydrazine decomposition reaction. The acidity of carriers plays a vital role on catalyst activity.

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## ՄԻԿՐՈԱԼԻՔԱՅԻՆ ԵՂԱՆԱԿՈՎ ԿՐԻՉՆԵՐԻ ՎՐԱ MO2C-Ի ՍԻՆԹԵԶԸ ԵՎ ԴՐԱ ԿԱՏԱԼԻՏԻԿ ԱԿՏԻՎՈԻԹՅԱՆ ՈԻՍՈԻՄՆԱՍԻՐՈԻԹՅՈԻՆԸ ՏԻԴՐԱԶԻՆՏԻԴՐԱՏԻ ՔԱՅՔԱՅՄԱՆ ՌԵԱԿՑԻԱՅՈԻՄ

#### Ա. Մ. ԱՂՈՅԱՆ, Ռ. Ա. ՄՆԱՑԱԿԱՆՅԱՆ և Դ. Ղ. ԴԱՎԹՅԱՆ

Իրականացվել է  $Mo_2C/4$ րիչ Համակարդերի սին/ժեղը միկրոալիջային եղանակով և դրանց կատալիտիկ Հատկու/ժյունների ուսումնասիրու/ժյունը՝ միկրոալիջային վառարանում։ Կատալիտիկ փորձարկումները իրականացվել են ՀիդրագինՀիդրատի ջայջայման ռեակցիայում։  $Mo_2C/4$ րիչ Համակարգերը ցուցաբերում են կատալիտիկ ակտիվու/ժյուն ջայջայման ռեակցիայում և կախված կիրառված կրիչի Հատկու/ժյուններից Համակարգի կատալիտիկ ակտիվու/ժյունը փոփոխվում է։ Ամենաբարձր կատալիտիկ ակտիվու/ժյունը դիտվել է  $Mo_2C/4 - Al_2O_3 / Հիդրագին ռեակցայիում (95.4%): Բոլոր դեպջերում Հիդրագի$ նի ջայջայումն ըն/ժացել է 100% ընտողականու/ժյամբ՝ ամոնիակի և ազոտի առաջացմամբ:

#### КАТАЛИТИЧЕСКИЕ СВОЙСТВА НАНЕСЕННОГО МО2С СИНТЕЗИРОВАННОГО МИКРОВОЛНОВОЙ РАДИАЦИЕЙ В РЕАКЦИИ РАЗЛОЖЕНИЯ ГИДРАЗИНГИДРАТА

#### А. М. АГОЯН, Р. А. МНАЦАКАНЯН и Д. А. ДАВТЯН

Институт химической физики им. А.Б.Налбандяна НАН Республики Армения Армения, 0014, Ереван, ул. П.Севака, 5/2 E-mail: artur.aghoyan@gmail.com

Изучены микроволновый синтез и каталитические процессы систем  $Mo_2C$  / носитель. Каталитические испытания были проведены по реакции разложения гидразинагидрата.  $Mo_2C$  на носителе показал каталитическую активность в реакции разложения. В зависимости от характеристик носителя она изменяется. Наибольшая каталитическая активность наблюдается при реакции с системой  $Mo_2C/\gamma$ - $Al_2O_3$  (95.4%). Во всех случаях разложение гидразина было на 100% селективным по отношению к аммиаку и азоту.

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