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INTEGRATED MICROWAVE SYNTHESIS AND CATALYTIC APPLICATION OF TRANSITION METAL CARBIDES FOR RAPID HYDRAZINE DECOMPOSITION

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Abstract: Microwave irradiation offers a unique strategy for combining fast catalyst preparation with intensive catalytic operation. Here, this concept was demonstrated by synthesizing microwave-active transition metal carbides within minutes and subsequently employing them in microwave-assisted hydrazine hydrate decomposition as a model reaction. The microwave-assisted method enabled rapid carbide formation and generated porous catalytic structures. Modification of β -Mo₂C with Cu notably enhanced its performance, with Cu-Mo₂C achieving 100% hydrazine conversion at 450 W (output power) within 3 min. Its exceptional activity was associated with the evenly distribution of Cu and the formation of accessible Cu-Mo₂C interfacial sites, whereas the comparable performance of single- and double-irradiated β -Mo₂C indicated that bulk phase purity alone did not affect catalytic efficiency. Instead, the results highlight the combined importance of surface organization, metal-carbide interfaces, and microwave-catalyst interactions. This integrated synthesis-catalysis strategy demonstrates how microwave prepared carbides can serve simultaneously as active heterogeneous catalysts and microwave absorbers, providing a promising platform for rapid and energy-efficient catalytic transformations.

Keywords: microwave-assisted synthesis; transition metal carbides; hydrazine decomposition; Cu-Mo₂C; microwave-active catalyst

Article Highlights:

Microwave irradiation provides rapid synthesis and catalytic use of transition metal carbides.

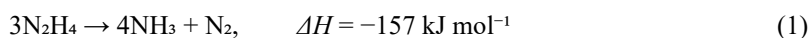
The Cu-Mo₂C compound provides complete conversion of hydrazine at 450 W within 3 minutes.

Uniform Cu distribution and available interfaces provide improved catalytic performance.

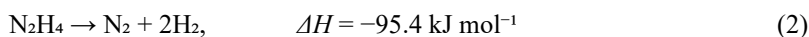
INTRODUCTION

The decomposition of hydrazine occupies a special place in heterogeneous catalysis, because one nitrogen-rich molecule can be transformed by two parallel pathways of direct technological importance. Depending on the catalyst and reaction conditions, hydrazine can form ammonia and nitrogen or decompose into nitrogen and hydrogen. Therefore, the reaction is important not only as a practical chemical transformation, but also as a sensitive model for examining how catalyst composition, surface structure, and energy transfer govern activity and reaction direction [1-4]. The method of ammonia formation underlies the established use of hydrazine in monopropellant systems for satellite attitude and orbit control [2], while the method of hydrogen formation offers a compact means of producing hydrogen on demand, with nitrogen as the only stoichiometric coproduct [3, 4]. This combination of practical value and competing chemistry composition makes the decomposition of hydrazine particularly suitable for evaluating new catalyst materials and nonconventional methods of catalytic activation.

The catalytic behavior of hydrazine is usually described by the following two general reactions. The ammonia-forming pathway proceeds as follows:



whereas the hydrogen-forming pathway proceeds as follows:



Efficient catalysts are essential for promoting rapid and selective hydrazine decomposition. The reaction rate reflects the ability of the catalyst surface to activate *N-N* and *N-H* bonds, while product selectivity is determined by the relative rates and sequence of these competing bond-cleavage pathways. Accordingly, the same reaction can be used to evaluate the efficiency of decomposition and, in combination with product analysis, the selectivity of the processes. In the present study, iodometric monitoring of hydrazine concentration provides a direct and convenient measurement of reaction progress and allows the catalytic performance of the synthesized materials to be compared.

Transition metal carbides (TMCs) represent an attractive platform for this chemistry. Since Levy and Boudart first described tungsten carbide as “platinum-like” in 1973, the catalytic properties of TMCs have been associated with the modification of the metal electronic structure by the introduction of carbon [5-7]. This interaction gives many carbides a combination of metallic conductivity, high reactant activation ability and adsorption properties that can resemble those of platinum group metals. Subsequently, TMCs have been investigated in hydrogenation, reforming, isomerization, hydroprocessing and electrochemical reactions, as well as in other transformations [6-11]. Their high thermal stability, mechanical strength, elevated melting points and comparatively accessible components further support their development as robust, non-noble catalytic materials [8, 9].

The catalytic properties of carbide are determined not only by its nominal composition but also by its crystalline phase, particle size, number of defects, open surface and interaction with carbonaceous or oxidized surface

species. These structural features are established during synthesis and can later evolve in the reaction environment. Thus, the preparation method is an integral part of catalyst design. Chemical vapor deposition, temperature-programmed reduction, carbothermal synthesis and self-propagating high-temperature synthesis were all used to produce TMCs with different phase compositions and morphologies [12-16]. The literature shows that control of heat and mass transfer during carburization plays a central role in the nucleation, phase development, particle growth and the formation of catalytically accessible interfaces [7, 13-17]. Microwave-assisted synthesis offers a particularly effective way to control this transformation. In contrast to conventional furnace heating, where heat is transferred from the reactor walls to the reaction mixture, microwave irradiation generates heat volumetrically through direct absorption of electromagnetic energy by microwave-responsive components. At the commonly used frequency is 2.45 GHz [18-20].

This method of energy delivery is well suited for the formation of carbides. Carbon-rich precursors can act as effective absorbers of microwave irradiation at the initial stage, rapidly converting electromagnetic energy into heat within the reacting solid. As carburization proceeds, the developing conductive carbide and carbide carbon phases may increasingly participate in microwave interaction. Rapid internal heating, short synthesis times and fast cooling can thereby influence nucleation and crystal growth and contribute to the appearance of nanoscale, defective, or interfacial structures that are valuable in heterogeneous catalysis [7, 18]. Microwave synthesis is thus more than a faster replacement for furnace treatment: it provides a distinct path for the conversion of carbon-containing precursors into catalytically functional carbide materials [22].

The same characteristics of materials that support microwave synthesis can also be useful during catalytic operation. Microwave-absorbing catalyst is dispersed in a weakly for microwave-absorbing reaction medium, electromagnetic energy is preferentially absorbed by the catalyst particles, resulting in localized heating at the catalyst surface and the solid–liquid interface. Preferential energy deposition can produce rapid catalyst heating, and under suitable field and heat transfer conditions, to localized areas with higher temperatures, which are often described as hot spots [19, 20]. Because heterogeneous reactions occur on the surface of the catalyst, such an interaction can intensify surface chemistry without requiring the entire reaction volume to follow the same heating profile.

Microwave irradiation has already been used for heterogeneous catalytic processes including hydrogenation, isomerization and dry reforming of methane [6, 10, 11]. Hydrazine hydrate decomposition under microwave conditions has also been demonstrated [1], which confirms the possibility of accelerating this reaction due to the interaction of microwaves with a catalyst. The deliberate strategy of synthesizing transition metal carbides (TMCs) by microwave irradiation and subsequently employing them as heterogeneous catalysts in microwave-assisted reactions remains largely unexplored, despite its potential to preserve the conductive and interfacial properties required for efficient electromagnetic energy coupling during catalysis.

Within this framework, the present work combines two successive steps using microwave irradiation. Transition metal carbides were synthesized by microwave irradiation, using carbon as main absorber at the beginning of carburization and forming carbide-containing products capable of interacting with the microwave field. The

resulting materials were then applied as catalysts for the decomposition of hydrazine hydrate under microwave irradiation, while the hydrazine concentration was monitored iodometrically.

The high decomposition performance observed for the microwave synthesized carbides is consistent with effective interaction between the catalyst and the microwave field. Carbide particles can act simultaneously as active heterogeneous surfaces and as localized energy-conversion regions, so that preferential heating near the catalyst-liquid interface enhances the rate of hydrazine conversion. This interpretation offers a coherent connection between the rapid formation of the carbide phases during synthesis and their performance during microwave-assisted catalysis. Future studies of dielectrics and local temperatures can further resolve the precise contribution of hot spots at the catalyst level, while the present reaction behavior provides a strong basis for this physically grounded explanation.

Accordingly, this study employs hydrazine decomposition as a model reaction to evaluate microwave-synthesized TMCs as microwave-absorbing heterogeneous catalysts. By integrating catalyst synthesis and catalytic application within a single microwave-based strategy, this work demonstrates a promising approach for rapid hydrazine conversion and the rational design of carbide catalysts for efficient microwave-assisted heterogeneous catalysis.

2. Experimental

2.1. Materials

For catalyst synthesis, the following reagents were used: ammonium paramolybdate tetrahydrate (Fisher Scientific, 99%), NiO (Sigma-Aldrich, 99.99%), CuO (Sigma-Aldrich, 99.99%), Co₃O₄ (Sigma-Aldrich, 99.5%), WO₃ (Sigma-Aldrich, ≥99%), NH₄VO₃ (Sigma-Aldrich, ≥99%), MoO₃ (Sigma-Aldrich, ≥99.5%), and carbon black (CABOT, Vulcan XC-72R). A 64 wt.% aqueous solution of hydrazine hydrate (Sigma-Aldrich) was used as the reactant.

The concentration of hydrazine during the reaction was determined by iodometric titration using a 0.1 N iodine solution (Sigma-Aldrich), 0.5 N hydrochloric acid (Sigma-Aldrich), sodium bicarbonate (NaHCO₃, Sigma-Aldrich, ≥99.5%), and deionized water.

2.2 Catalyst Synthesis

2.2.1. General microwave-assisted procedure

The carbide precursors were mixed in the stoichiometric ratios shown in Table 1. Each precursor mixture was manually ground in an agate mortar for 10 min to obtain a homogeneous powder. The mixture was transferred to a quartz reactor and initially distributed over the inner wall of the reactor. Before microwave treatment, the reactor was purged with high purity N₂ (99.99%) for about 20 min. The reactor was then positioned vertically so that the powder collected at the bottom.

Microwave-assisted synthesis was carried out in a modified household microwave oven (Electrolux EMS 2820) operating at 2.45 GHz and an output power of 900 W. A continuous nitrogen flow of 25 mL min⁻¹ was maintained throughout irradiation. Each primary carbide synthesis was conducted for 10 min. Depending on the composition and microwave exposure of the precursor mixture, the sample temperature was approximately 900-1100 °C. Temperature was monitored through a hole in the back wall of the microwave cavity using an optical pyrometer (Dostmann HT-1800).

Table 1. Stoichiometric amounts of starting materials required for the synthesis of catalysts

No.	Catalyst	C, g	NH ₄ VO ₃ , g	WO ₃ , g	MoO ₃ , g	CuO, g	Co ₃ O ₄ , g	NiO, g	Reaction
1	VC	6.6	18.57	-	-	-	-	-	2NH ₄ VO ₃ +7C=2VC+2NH ₃ +H ₂ O+5CO
2	WC	1.22	-	5.92	-	-	-	-	WO ₃ +4C=WC+3CO
3	β-Mo ₂ C mono	2.06	-	-	7.06	-	-	-	2MoO ₃ +7C=Mo ₂ C+6CO
4	10% Ni-Mo ₂ C	1.97	-	-	-	-	-	0.60	3NiO+4C=Ni ₃ C+3CO
5	10% Cu-Mo ₂ C	1.89	-	-	6.35	0.625	-	-	CuO+C=Cu+CO
6	10% Co-Mo ₂ C	2.01	-	-	6.65	-	0.64	-	Co ₃ O ₄ +5C=Co ₃ C+4CO
7	20% Mo ₂ C/C	2.65	-	-	0.85	-	-	-	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O→6NH ₃ +7MoO ₃ +7H ₂ O
8	5% Mo ₂ C/C	2.91	-	-	0.211	-	-	-	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O→6NH ₃ +7MoO ₃ +7H ₂ O

2.2.2. Preparation of β -Mo₂C and metal-modified Mo₂C catalysts

β -Mo₂C was prepared from MoO₃ and carbon according to the general microwave-assisted procedure and the stoichiometry given in Table 1. When further treatment was required to complete carburization, the initially obtained material was reground to restore homogeneity and subjected to additional microwave treatment under the same nitrogen atmosphere. The materials obtained after one and two cycles of microwave treatment are indicated as Mo₂C-mono and Mo₂C-double, respectively. The mono-treated sample was used as the β -Mo₂C support for subsequent metal modification.

The catalysts Ni-Mo₂C, Cu-Mo₂C, and Co-Mo₂C were synthesized according to the reaction schemes presented in Eqs. (3,4), (3,5), and (3,6), respectively (Table 1), with the dopant metal content adjusted to 10 wt.% in the final material based on the stoichiometric composition. The presence and distribution of the added metals were evaluated by energy dispersive X-ray spectroscopy; formation of a separate nickel-containing crystalline phase was not determined by XRD.

2.2.3. Preparation of supported Mo₂C/C catalysts

The supported catalysts containing 5 wt.% and 20 wt.% Mo₂C on carbon (Mo₂C/C) were synthesized in accordance with the stoichiometric ratios defined by reactions (3,7,8).

The materials were prepared via a wet impregnation method. An aqueous solution of ammonium paramolybdate was used as the molybdenum precursor and impregnated onto carbon black (Vulcan XC-72R) in an amount corresponding to the desired final Mo₂C loading (5 wt.% and 20 wt.%). The suspension was thoroughly mixed to ensure uniform distribution of the precursor over the carbon surface.

The impregnated samples were then dried at 110 °C for 4 h to remove excess moisture. Subsequently, microwave-assisted carburization was performed under conditions analogous to those used for bulk carbide synthesis, yielding Mo₂C nanoparticles supported on carbon.

2.3. Catalytic experiments

The decomposition of hydrazine hydrate was carried out by microwave irradiation in a special closed Teflon reactor placed inside the modified microwave oven (Fig. 1). Microwave output powers of 180-600 W and irradiation times of 2-4 min were investigated.

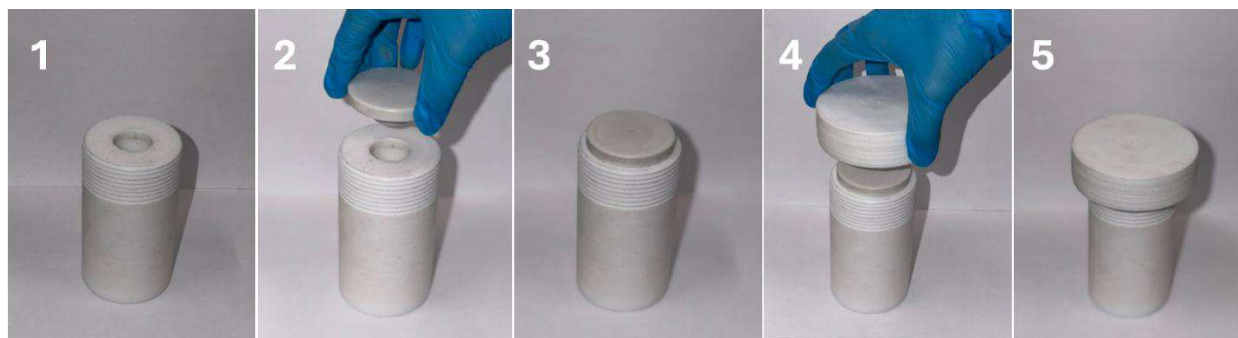


Fig. 1 Teflon reactor used for microwave-assisted hydrazine decomposition

In a typical experiment, 0.100 g of catalyst was placed in the reactor and 5.0 mL of a 2 wt.% aqueous solution of hydrazine-hydrate was added. The reactor was closed and irradiated at the selected power and reaction time. Immediately after irradiation, the reactor was immersed in a water bath and cooled rapidly to room temperature. After cooling, the reactor was opened and 20.0 mL of distilled water was added to the reaction mixture. The resulting suspension was transferred to a test tube and filtered to remove the solid catalyst. Residual hydrazine in the clear filtrate was quantified by iodometric titration.

2.3.1. Iodometric determination of residual hydrazine

For the iodometric procedure a 2.5 mL portion of the filtrate was transferred to an Erlenmeyer flask and diluted with distilled water to a total volume of 18.5 mL. The diluted solution was divided into three equal parts for repeated titration. To each portion, 5.0 mL of 0.5 N HCl and 1.0 g of NaHCO₃ were added, after which the solution was titrated with standardized 0.1 N iodine solution.

Quantitatively, hydrazine reacts with iodine according to:



Thus, one mole of hydrazine consumes two moles of iodine. The residual hydrazine concentration was obtained from the mean iodine consumption of the three aliquots, after application of the corresponding dilution factors. The conversion of hydrazine was calculated relative to an untreated solution of the same initial concentration:

$$\text{Conversion (\%)} = \frac{C_0 - C}{C_0} \times 100\% \quad (4)$$

C₀-concentration of hydrazine hydrate before the microwave treatment

C-concentration of hydrazine hydrate after the reaction (residual concentration of hydrazine hydrate).

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Rotaflex D/max-RC diffractometer with Cu K α radiation ($\lambda=1.54056$ Å). Data were collected over the 2θ range 10-80° with a step size of 0.02°. Crystalline phases were identified using MDI JADE software and the corundum-number method.

The morphology of the particles and their elemental composition were examined using a Thermo Fisher Scientific Prisma E scanning electron microscope equipped for energy-dispersive X-ray spectroscopy (SEM-EDS). Instrumental operating conditions were those specified in the corresponding experimental records. EDS was used to confirm the presence of the modifying metals, whereas phase distribution were based on XRD only when distinct crystalline reflections were observed.

3. Results and discussion

3.1 XRD characterization

X-ray powder diffraction (XRD) analysis was performed to identify the phase composition of the synthesized carbides and their doped counterparts. The processed XRD patterns of β -Mo₂C samples obtained via microwave-assisted synthesis are presented in Fig. 2a and 2b for the Mo₂C-mono and Mo₂C-double samples, respectively (Table 1, Eq. 3).

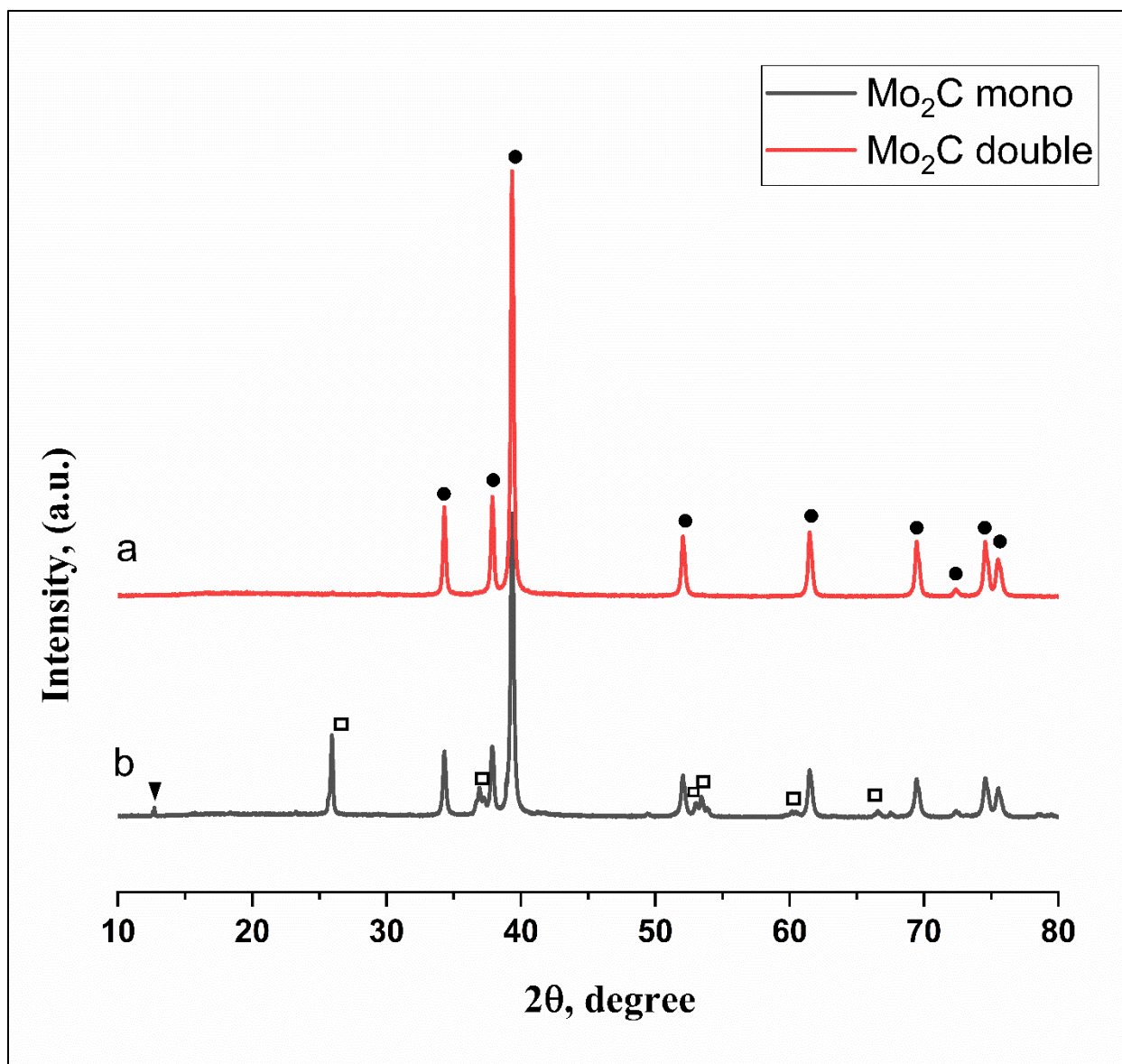


Fig. 2 β - Mo_2C XRD diffractograms obtained after (a) two successive microwave treatments (Mo_2C -double) and (b) one microwave treatment (Mo_2C -mono). The symbols indicate the corresponding crystalline phases: (▼) – MoO_3 , (□) – MoO_2 , (●) – Mo_2C

Fig. 2 (a,b) presents the processed XRD diffractograms of β - Mo_2C mono- and double samples synthesized via the microwave-assisted method (Table 1, Eq. 3).

For the β - Mo_2C - mono sample (Fig. 2b), the diffraction pattern exhibits characteristic reflections of β - Mo_2C (PDF No. 35–0787) at 2θ values of 34.32° , 37.9° , 39.35° , 52.09° , 61.52° , 69.5° , and 74.6° , corresponding to the (100), (002), (101), (102), (110), (103), and (112) crystallographic planes, respectively. In addition to the carbide phase, diffraction peaks attributable to MoO_2 (PDF No. 65–5787) are observed at approximately $2\theta \approx 25.93^\circ$, 36.88° , 53.07° ,

53.48°, and 66.65°, corresponding to the (011), (211), (222), (311), and (402) planes. Minor contributions from MoO₃ (PDF No. 05–0508) are also detected, with a characteristic reflection at $2\theta \approx 12.73^\circ$ assigned to the (020) plane.

In contrast, the XRD pattern of the β -Mo₂C-double sample (Fig. 2a) shows only reflections corresponding to β -Mo₂C (PDF No. 35–0787), with no detectable oxide-related peaks. The diffraction maxima appears at the same 2θ positions as in the β -Mo₂C-mono sample, confirming the preservation of the carbide crystal structure while indicating complete conversion of oxide precursors during the secondary microwave irradiation.

Fig. 3(a, b, c) presents the comparative XRD patterns of β -Mo₂C doped with transition metals. In the diffractograms of all three samples, characteristic peaks of Mo₂C (PDF# 35-0787) are clearly observed at 2θ values of approximately 34.40°, 37.97°, 39.39°, 52.10°, 61.60°, 69.52°, 72.71°, 74.61°, and 75.76°, corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystal planes, respectively.

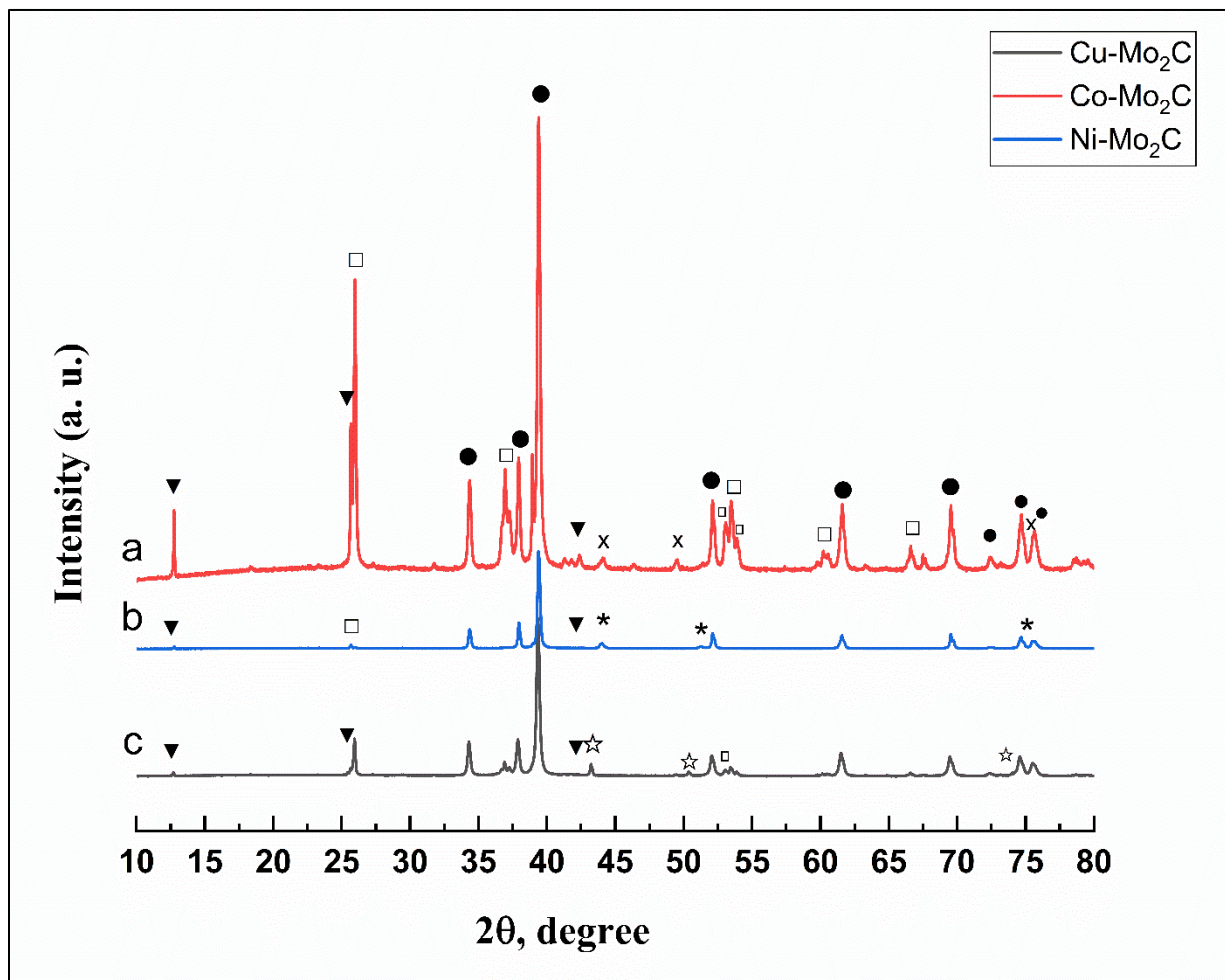


Fig. 3 XRD patterns of the metal-modified Mo₂C catalysts: (a) Co-Mo₂C, (b) Ni-Mo₂C, and (c) Cu-Mo₂C. The symbols indicate the corresponding crystalline phases: (▼) – MoO₃, (□) – MoO₂, (●) – Mo₂C, (☆) – Cu, (x) – Co, (*) – Ni

Additionally, peaks corresponding to MoO_3 (PDF No. 35-0609) are present at 2θ values of 12.820° and 25.74° , which are attributed to the (020) and (040) planes.

In the XRD diffractograms of Cu-Mo₂C (Fig. 3c) and Co-Mo₂C (Fig. 3a), additional peaks corresponding to MoO_2 (PDF No. 65-5787) are observed at 2θ angles of approximately 25.94° , 36.89° , 37.66° , 53.12° , 53.47° , and 53.96° , which correspond to the (100), (-211), (-213), (-222), (-311), and (112) planes, respectively. In the diffractogram of Ni-Mo₂C (Fig. 3b), a MoO_2 -related peak is also present at $2\theta \approx 25.94^\circ$, corresponding to the (100) plane.

The processed XRD patterns also reveal the presence of characteristic peaks of the respective dopant metals in each catalyst. In the Cu-Mo₂C diffractogram (Fig. 3c), copper peaks are observed at $2\theta \approx 43.297^\circ$, 50.433° , and 74.130° , corresponding to the (111), (200), and (220) planes of metallic copper (PDF No. 04-0836), indicating the presence of metallic Cu in the sample. In the diffractogram of Ni-Mo₂C (Fig. 3b), weak-intensity peaks appear at approximately $2\theta \approx 44.347^\circ$, 51.673° , and 76.095° , which match the (111), (200), and (220) planes of metallic Ni (PDF# 65-0380) [21]. Similarly, in the Co-Mo₂C diffractogram (Fig. 3a), cobalt peaks are detected at $2\theta \approx 44.216^\circ$, 51.522° , and 75.853° , corresponding to the (111), (200), and (220) planes of metallic Co (PDF No. 15-0806).

A comparative analysis of the XRD patterns indicates that, in all samples except $\beta\text{-Mo}_2\text{C}$ -double, diffraction peaks corresponding to molybdenum oxide phases are present, differing primarily in their relative intensities. This suggests that the extent of carburization varies among the samples, with residual oxide content remaining to different degrees depending on the synthesis conditions.

In the case of the doped (metal-modified) Mo₂C samples, additional diffraction peaks corresponding to the metallic phases of the introduced dopants are observed. Among these, the copper-containing sample exhibits relatively higher intensity reflections associated with metallic Cu. This may indicate a higher degree of crystallinity and/or larger coherent domain size of the copper phase compared to other dopants.

3.2 Morphology and elemental distribution

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were also used to investigate the morphology and surface elemental composition of the synthesized samples (Mo₂C mono, Mo₂C double, Cu-Mo₂C, Ni-Mo₂C, and Co-Mo₂C).

SEM images of the Mo₂C samples (Fig. 4 a, b) reveal that the surface is predominantly composed of a highly porous, cotton-like morphology. This structure is characteristic of $\beta\text{-Mo}_2\text{C}$ formed under rapid microwave-assisted synthesis conditions and consists of agglomerated nanograins distributed throughout the material. For the metal-modified samples (Fig. 4 c-g), the cotton-like Mo₂C matrix is preserved; however, distinct morphological differences are observed depending on the dopant. For example, in the Ni-Mo₂C and Co-Mo₂C samples, additional spherical particles of varying size are present and are unevenly distributed across the surface. A magnified image (Fig. 4 d, g)

suggests that these spherical features originate from localized melting and subsequent solidification during microwave irradiation.

In contrast, the Cu–Mo₂C sample (Fig. 4 e, f) exhibits a homogeneous, porous, cotton-like morphology without the presence of large or spherical segregated particles. The grain size within this structure is estimated to be below 100 nm. Also, EDS mapping (Fig. 5 c) confirms that copper is uniformly distributed throughout the Mo₂C matrix.

Those correlated with XRD results show that these observations support the conclusion that copper is more evenly dispersed within the Mo₂C structure, whereas nickel and cobalt tend to segregate into separate phases. This structural distinction is consistent with catalytic performance data, where the Cu–Mo₂C catalyst demonstrates superior activity in the model reaction of hydrazine hydrate decomposition (Fig. 7), likely due to the higher availability of accessible active sites.

EDS analysis (Fig. 5) indicates a significantly higher oxygen content in the Mo₂C-mono sample compared to the Mo₂C-double sample, which is consistent with XRD results showing the presence of residual oxide phases after a single microwave treatment. In the double-step sample, the oxygen content is markedly reduced; the remaining oxygen is likely associated with surface oxidation due to exposure to ambient conditions, which is typical for highly reactive carbide surfaces.

Fig. 5 (d, e) shows that, in the Co–Mo₂C and Ni–Mo₂C samples, nickel and cobalt are predominantly concentrated within these spherical particles, while the surrounding cotton-like Mo₂C matrix contains little to no detectable dopant. This indicates that Ni and Co are not uniformly dispersed on the Mo₂C surface but instead segregate into distinct metal-rich domains. Notably, the spherical particles are smaller and less pronounced in the Co–Mo₂C sample compared to the Ni–Mo₂C system, suggesting differences in metal mobility and phase formation behavior under microwave conditions.

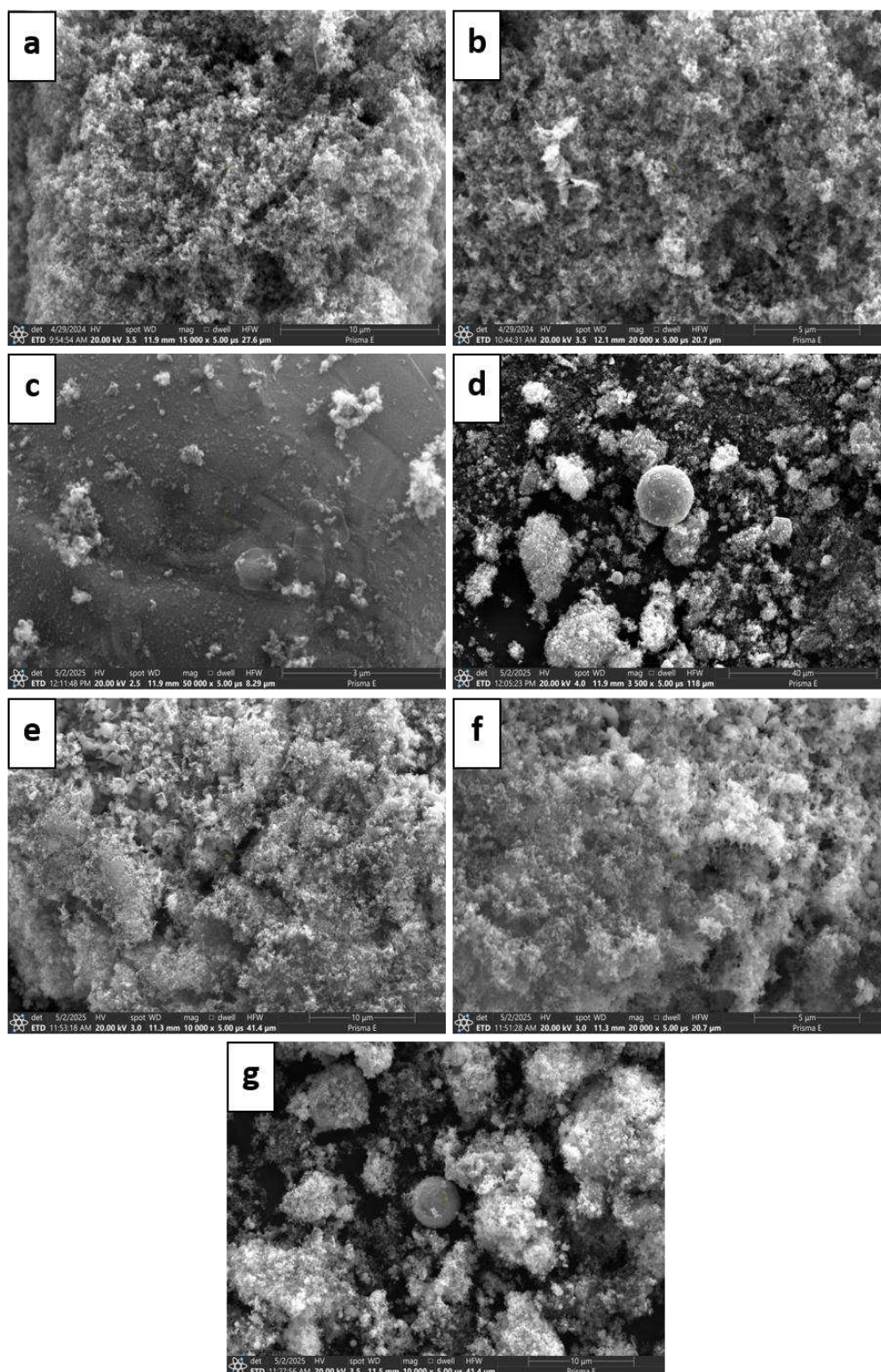


Fig. 4 SEM analysis results of (a) β -Mo₂C mono and (b) β -Mo₂C double and molybdenum carbide doped with different transition metals: (c, d) Ni-Mo₂C; (e, f) Cu-Mo₂C; (g) Co-Mo₂C

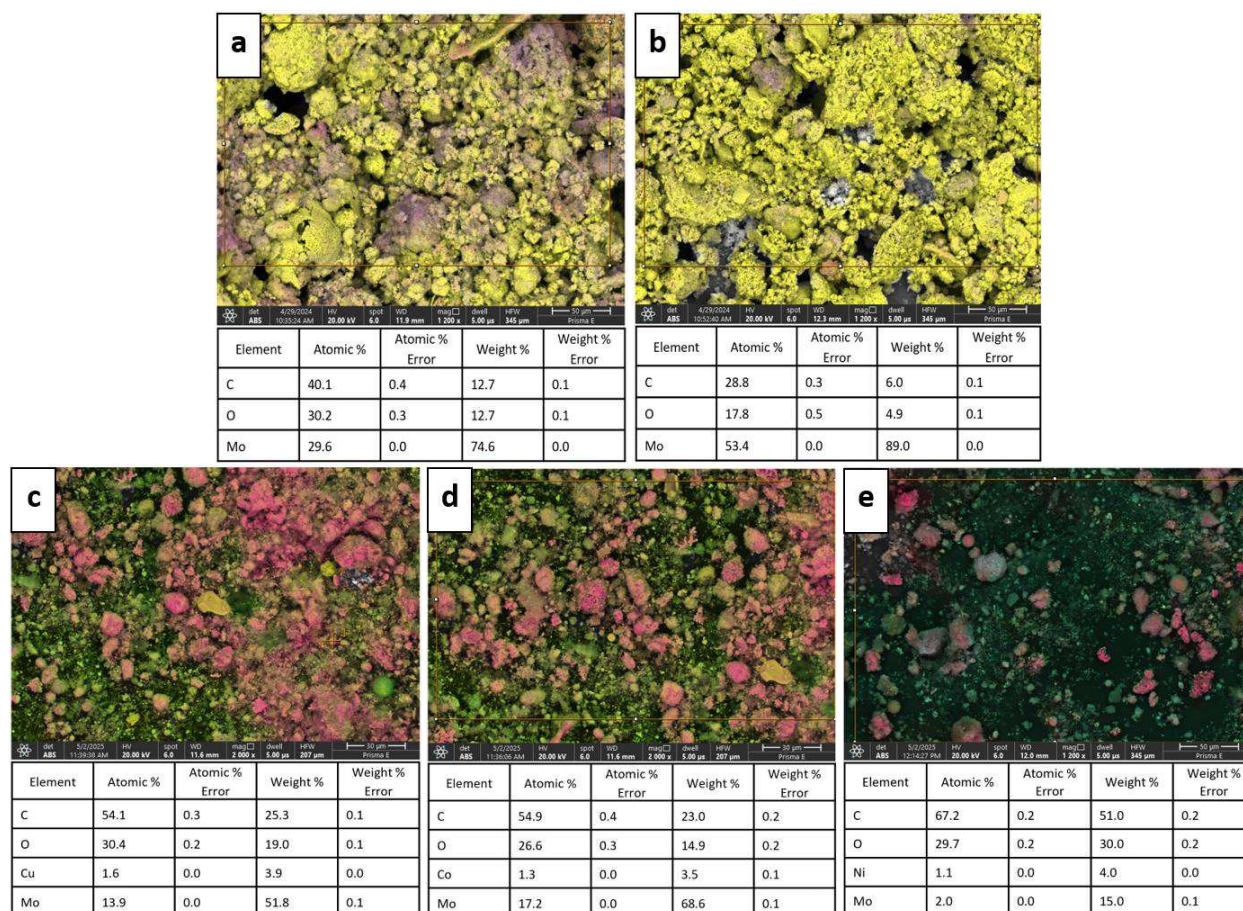


Fig. 5 EDS analysis results of (a) β -Mo₂C mono and (b) β -Mo₂C double and molybdenum carbide doped with different transition metals: (c) Cu- Mo₂C, (d) Co- Mo₂C, (e) Ni- Mo₂C

3.3. Microwave-assisted decomposition of hydrazine hydrate

3.3.1. Screening of carbide catalysts

The microwave-assisted decomposition of hydrazine hydrate was first evaluated over Mo₂C-mono, Mo₂C-double, 5 wt.% Mo₂C/C, 20 wt.% Mo₂C/C, VC, and WC. The catalysts were tested using 0.1 g of material and 5 mL of 2 wt.% aqueous hydrazine hydrate for 4 min at nominal power settings between 180 and 600 W. The microwave unit contained a 900 W; therefore, the lower nominal powers were produced by duty-cycle modulation rather than by continuous irradiation at the stated power.

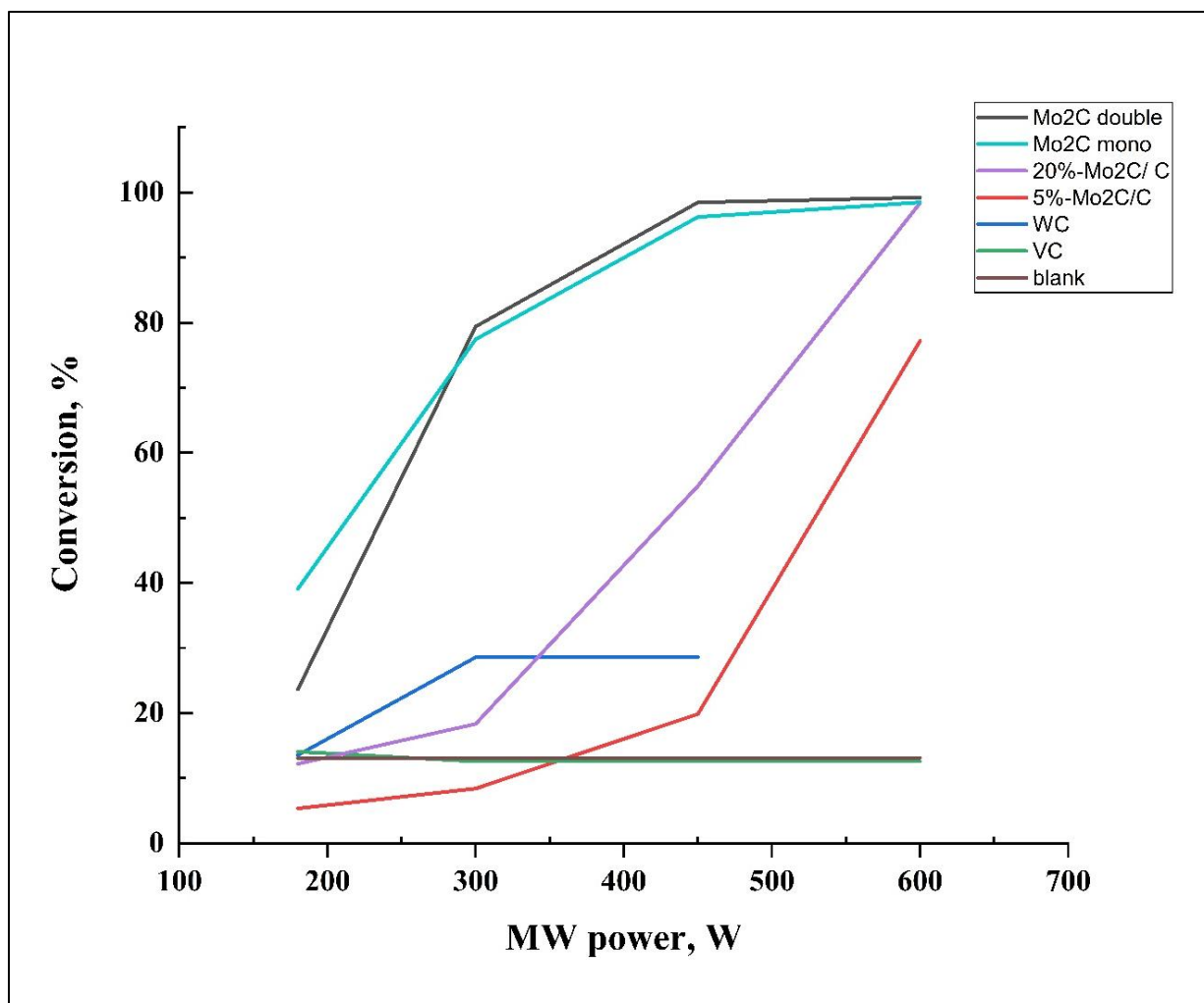


Fig. 6 Effect of nominal microwave power on hydrazine conversion over Mo₂C-double, Mo₂C-mono, 5 wt.% Mo₂C/C, 20 wt.% Mo₂C/C, VC, and WC (catalyst mass: 0.1 g; reaction time: 4 min; nominal power: 180–600 W)

VC and WC exhibited comparatively low conversion and were not selected for further optimization. Both bulk β -Mo₂C catalysts were substantially more active and reached approximately 96% conversion at 450 W after 4 min (Fig. 6). The high and nearly identical conversions obtained with Mo₂C-mono and Mo₂C-double are noteworthy because their crystalline phase compositions differ markedly: Mo₂C-mono contains residual MoO₂/MoO₃, whereas Mo₂C-double is phase-pure β -Mo₂C within the XRD detection limit.

In particular, the β -Mo₂C-mono sample contains residual molybdenum oxide phases, whereas the β -Mo₂C-double sample consists of phase-pure β -Mo₂C. Previously, Aghoyan et al. reported that β -Mo₂C-mono exhibited higher catalytic activity than the double catalyst in the hydrogenation of naphthalene performed under conventional thermal heating conditions [6]. The different behavior observed under microwave irradiation suggests that catalytic performance is governed not only by phase purity or the total number of active sites, but also by the nature of microwave–surface interactions. It can be assumed that microwave irradiation promotes the formation and/or energetic

activation of localized surface “hot spots” associated with structural defects and heterogeneous surface regions. Under such conditions, the defect structure and microwave absorption characteristics of the catalyst surface may play a more decisive role than the overall concentration of catalytically active phases. Since both β -Mo₂C samples possess similar defect-rich porous morphologies, their catalytic activities under microwave irradiation become comparable despite differences in oxide content.

To further examine this assumption, transition metal-doped Mo₂C catalysts were investigated in the model reaction of hydrazine hydrate decomposition. Based on literature data [23], together with the XRD, SEM, and EDS results obtained in the present study, it was hypothesized that both the accessibility and spatial distribution of metallic active centers under microwave irradiation significantly influence catalytic performance.

3.3.2. Effect of metal modification

The role of metal identification and distribution was examined using Cu-Mo₂C, Co-Mo₂C, and Ni-Mo₂C under the same catalytic conditions (180–600 W, 2–4 min). As shown in Fig. 7, Cu-Mo₂C demonstrated the highest catalytic activity, achieving complete hydrazine conversion (100%) at 450 W, with no significant further changes at higher power. Co-Mo₂C also demonstrated high activity, reaching approximately 97% conversion at 600 W. In contrast, Ni-Mo₂C showed substantially lower performance, with a maximum conversion of only 38% even at 600 W. These results correlate well with the structural and morphological observations obtained from SEM/EDS analysis. In the Cu-Mo₂C catalyst, copper is uniformly distributed throughout the porous cotton-like Mo₂C matrix without the formation of large segregated particles (Fig. 4 e, f), providing a high density of accessible active sites under microwave irradiation. In the Co-Mo₂C system, although some spherical segregated regions are present, cobalt remains relatively well distributed throughout the structure (Fig. 4 g), resulting in intermediate catalytic activity. Conversely, in the Ni-Mo₂C sample, nickel is predominantly concentrated within isolated spherical domains (Fig. 4 c, d), leading to poor dispersion within the Mo₂C matrix and consequently lower catalytic efficiency.

Thus, the catalytic studies confirm the structural conclusions derived from XRD, SEM, and EDS analyses and demonstrate that the uniform distribution of microwave-active metallic centers within the Mo₂C structure is a key factor governing catalytic performance in hydrazine decomposition under microwave irradiation. Based on these results, Cu-Mo₂C was identified as the most effective catalyst, and subsequent investigations focused on evaluating the influence of microwave irradiation time and catalyst loading on hydrazine conversion.

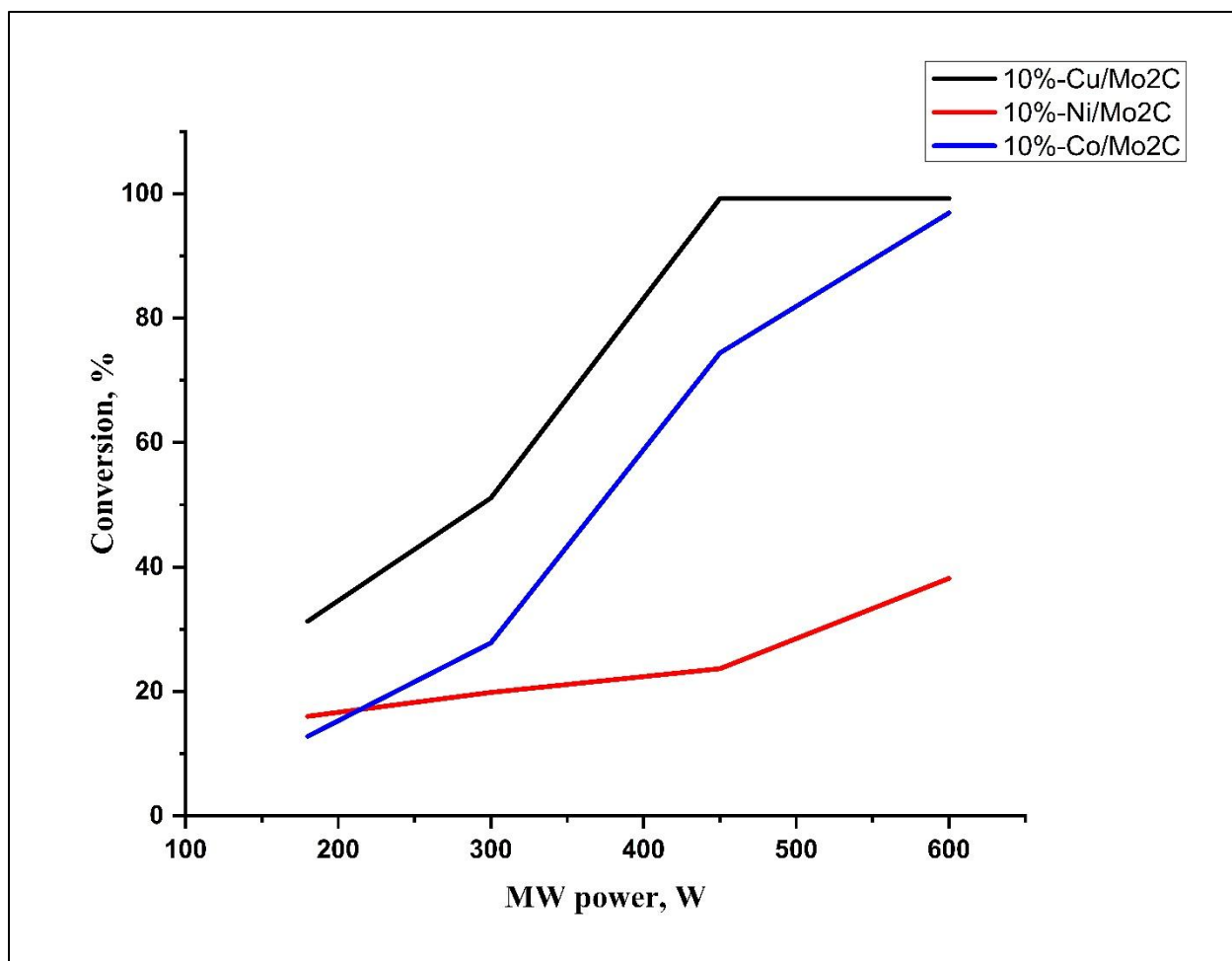


Fig. 7 Hydrazine hydrate conversion dependence on microwave power and catalyst type: (catalyst mass: 0.1 g; reaction time: 4 min; nominal power: 180-600 W)

3.3.3. Optimization of irradiation time and catalyst amount

After catalyst screening, Cu-Mo₂C was selected to determine the minimum irradiation time required at 450 W. The conversion of hydrazine increased continuously between 2 and 3 min and reached 100% after 3 min (Fig 8). Extending the irradiation period to 4 min produced no further change because the analytical limit of complete conversion had already been reached. This result demonstrates that the optimized catalyst achieves complete decomposition of the hydrazine in a short time of microwave treatment.

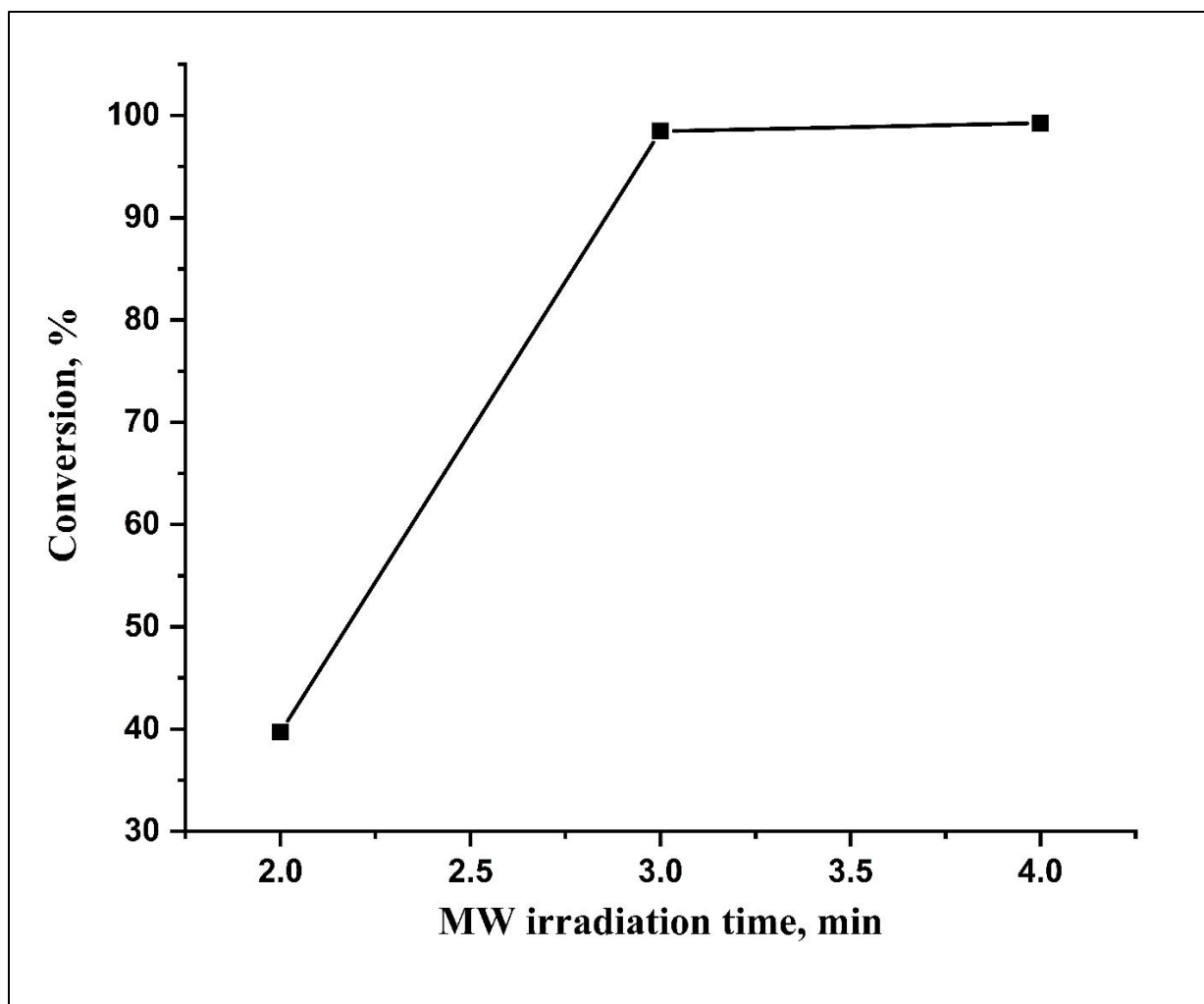


Fig. 8 Conversion of hydrazine hydrate as a function of microwave irradiation time (Cu/Mo₂C catalyst mass: 0.1 g; nominal power: 450 W; reaction time: 2-4 min)

Catalyst-loading experiments were subsequently performed at 450 W for 4 min (Fig. 9). Conversion increased as the Cu-Mo₂C amount was raised from 50 mg and reached 100% at 100 mg. Increasing the catalyst amount to 200 mg did not improve the measured conversion because all hydrazine had already been consumed at 100 mg. Thus, under the conditions used, 0.1 g represents the lowest tested catalyst load, which provided complete conversion within 4 min.

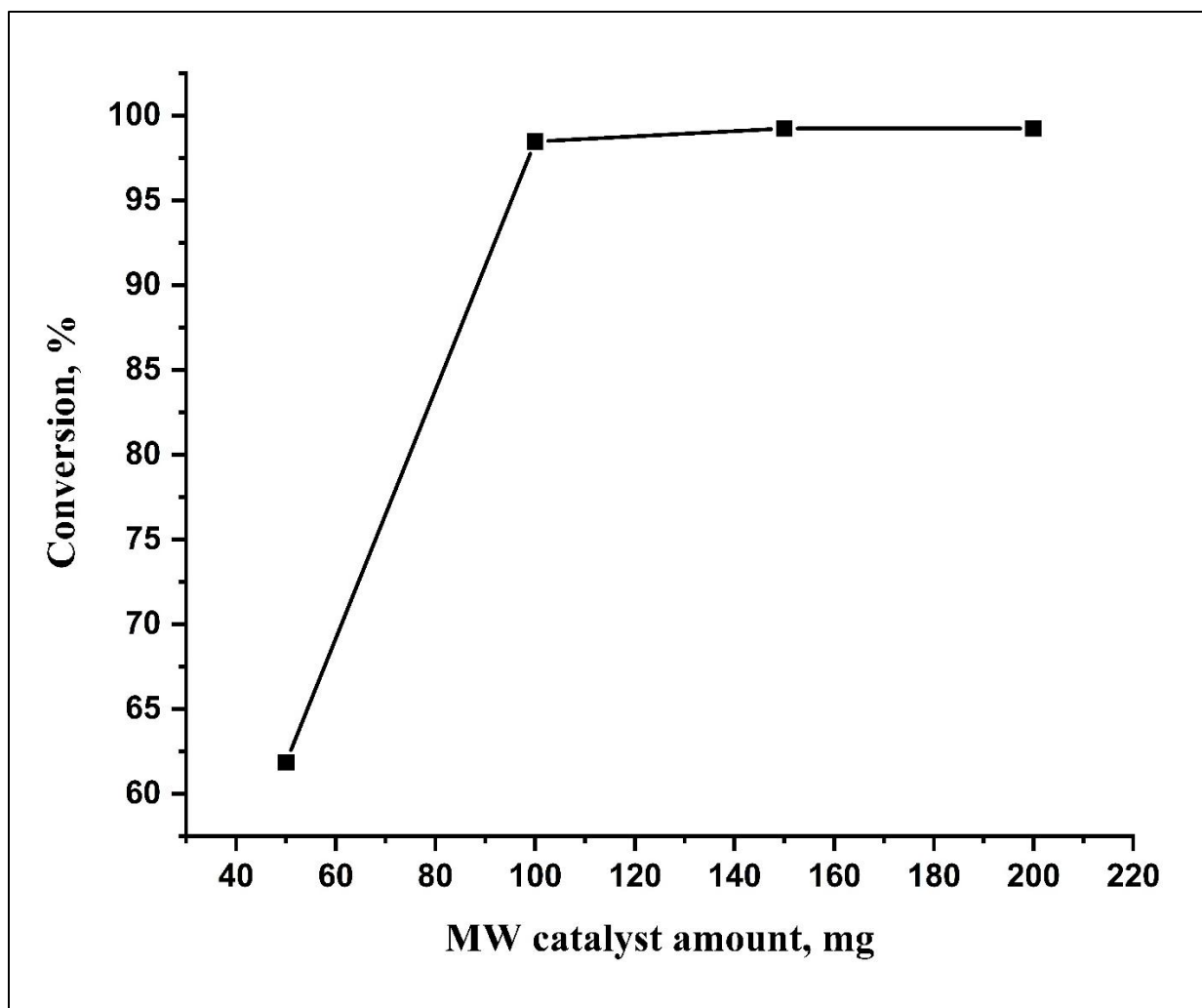


Fig. 9 Dependence of hydrazine hydrate conversion on the amount of Cu/Mo₂C catalyst (catalyst mass: 50-200 mg; nominal power: 450 W; reaction time: 4 min)

3.4. Integrated interpretation and significance of the process

Taken together, the structural and catalytic results show that microwave-prepared Mo₂C is effective not only as a heterogeneous catalyst but also as solid reacting to microwave irradiation during the decomposition of hydrazine. The first microwave treatment rapidly forms a porous and highly defective β -Mo₂C-rich material, while the second treatment completes carburization without destroying the open morphology. However, during catalysis the nearly identical characteristics of Mo₂C-mono and Mo₂C-double shows that the maximum purity of the bulk phase is not a necessary condition for high conversion of hydrazine under microwave irradiation.

Metal modification reveals a second controlling factor: accessible distribution of the added metal over the carbide matrix. Cu-Mo₂C combines the porous structure of Mo₂C, which is sensitive to microwave irradiation, with the most homogeneous metal distribution and consequently provides the highest conversion at the lowest effective power among the modified catalysts. By contrast, segregation of Ni from the Mo₂C support into large Ni-rich regions

is accompanied by noticeably lower catalytic activity. This relationship highlights the importance of maximizing metal-carbide interfacial contact rather than considering only nominal composition.

Presumably, the carbide matrix absorbs microwave energy and generates rapid localized heating in close proximity to catalytic surface sites, while the dispersed metal domains modify hydrazine activation at the interface. Structural defects, residual oxygen-containing particles on the surface and metal-carbide boundaries can affect the work surface. This interpretation is consistent with the observed dependence on the type of carbide, metal dispersion, microwave power, irradiation time, and catalyst loading.

As part of this work, the principal result of the study is the complete conversion of a 2 wt.% hydrazine hydrate solution using 0.1 g Cu-Mo₂C at a nominal microwave power of 450 W within 3 min. The combined microwave synthesis and catalytic application establish a compact process in which the carbide material is first formed rapidly by microwave irradiation and is subsequently used as the microwave-responsive catalytic phase. This dual application is the central technological feature of the work.

4. Conclusion

An integrated microwave approach was developed for the rapid synthesis of transition metal carbides and their subsequent use in the decomposition of hydrazine hydrate using microwave irradiation. The synthesized porous carbide catalysts, sensitive to microwave irradiation, showed high activity, while Cu-Mo₂C ensured the complete conversion of hydrazine at 450 W for 3 minutes. Their excellent performance was associated with the uniform distribution of Cu and the formation of accessible Cu-Mo₂C interfacial sites. The results show that microwave-synthesized carbides can function simultaneously as heterogeneous catalysts and efficient microwave absorbers, contributing localized energy deposition at the active surface. This combined synthesis-catalysis strategy provides a promising platform for fast and energy efficient catalytic transformations.

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