

# Mo and W Carbide: Tunable Catalysts for Liquid Phase Conversion of Alcohols

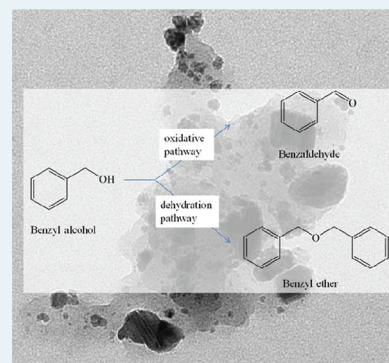
Alberto Villa,<sup>\*,†</sup> Sebastiano Campisi,<sup>†</sup> Cristina Giordano,<sup>‡</sup> Katharina Otte,<sup>‡</sup> and Laura Prati<sup>\*,†</sup>

<sup>†</sup>Dipartimento di Chimica, Università degli Studi di Milano, Via Venezian 21, I-20133 Milano, Italy

<sup>‡</sup>Department of Colloid Chemistry, Max-Planck-Institute of Colloids and Interfaces, Research Campus Golm, D-14424 Potsdam, Germany

## S Supporting Information

**ABSTRACT:** The application of Mo and W carbide (Mo<sub>2</sub>C and WC respectively) in the liquid phase oxidation of benzyl alcohol has been presented. Mo<sub>2</sub>C and WC are, indeed, considered among the most suitable candidates to replace noble metals for oxidation reactions because of their well recognized Pt- and Ru-like behavior, respectively. The good activity of metal carbides and their low cost, compared with noble metals, makes them appealing systems, worth of further investigations. Moreover, the peculiar tunability of the selectivity of these catalysts depending on the reaction medium has been highlighted.



**KEYWORDS:** metal carbides, selective oxidation, alcohols

Liquid phase oxidation of alcohols using based heterogeneous catalyst is an important process in green chemistry.<sup>1,2</sup> A lot of effort has focused in recent years on the development of new clean processes using supported noble metals as catalysts and molecular oxygen as oxidant.<sup>1–3</sup> However, in order to decrease the cost and favor a rapid industrial application, different catalytic systems, based on less expensive transition metal oxides have to be developed. In particular, it has been shown that metal carbides present a “noble-metal-like” structure.<sup>4–6</sup> WC and Mo<sub>2</sub>C possess an electronic structure similar to Pt and Ru, respectively, thus representing good candidates to replace such noble metals in their catalytic processes. Particularly, Mo<sub>2</sub>C and WC have attracted a lot of attention as catalytic materials because of their physical and chemical properties, including mechanical strength and durability; thermal stability; high resistance to sintering; and, in particular, catalytic performance.<sup>7,8</sup> Mo<sub>2</sub>C has been already proved to be active in noble metal-catalyzed reactions, such as ammonia synthesis and decomposition, aromatization, methane reforming, hydrogenation, and hydrodesulfurization.<sup>9–12</sup>

The synthesis methodologies of metal carbide can be divided into physical methods, such as laser ablation, arc-discharge, and evaporation; and chemical methods, such as direct carbonation of the elements and carbonation of the corresponding metal oxides.<sup>13–15</sup> However, these methods need preliminary treatments or postsynthesis purification, and often, the nanoparticles obtained are not crystalline and not small enough (size >50 nm) for catalytic application.

A versatile route for the synthesis of metal carbide nanoparticles using urea as the carbon source was reported in recent years.<sup>16</sup> The metal carbides obtained by this route are highly crystalline, with an average particle diameter of 2–6 nm for WC and 15–30 nm for Mo<sub>2</sub>C. Herein, we tested Mo and W carbide in the liquid phase oxidation of alcohols to replace the catalytic systems based on precious and expensive metals, such as Pt or Pd. Benzyl alcohol was used as the model alcohol, and the stability of the carbides under the operative conditions has been examined.

Mo and W carbides have been synthesized with the procedure reported in ref 16, and their properties are reported in Table 1.

An appropriate amount of ethanol was added to the solid metal precursor (MoCl<sub>5</sub> or WCl<sub>4</sub>), forming the corresponding metal orthoesters. Solid urea was then added to the alcoholic solution, and the urea gels obtained were heated at 800 °C for 3 h under N<sub>2</sub> gas flow. XRD diffractograms (Figure 1) showed the crystalline structure of Mo (ICDD 00-011-0680) and W carbides (WC, ICDD 00-025-1047; W<sub>2</sub>C, ICDD 00-035-0776), and a mean particle size of 18 and 10 nm, respectively, was confirmed through the Scherrer equation (Table 1).

The generated pHs of the metal carbides were 2.8 and 3.2 for Mo and W carbide, respectively (Table 1).

Received: April 12, 2012

Revised: May 22, 2012

Published: June 1, 2012

**Table 1.** BET, XRD and acid base titration of metal carbides before catalytic tests

sample	diameter XRD (nm)	surface area (m <sup>2</sup> /g)	generated pH
Mo <sub>2</sub> C	18	25	2.8
WC	10	78	3.2

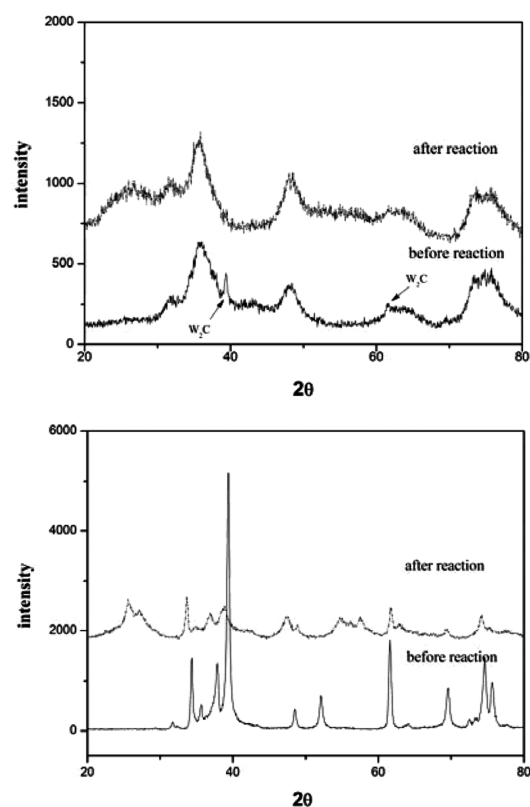
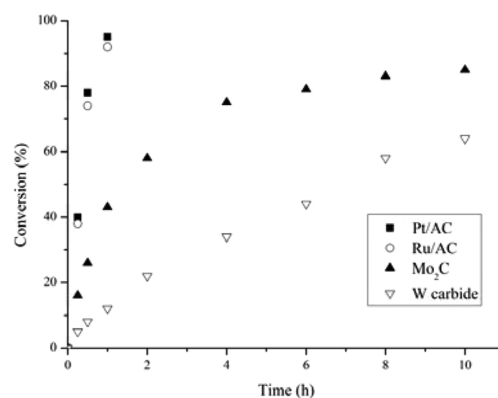
The catalytic test has initially been carried out under solventless conditions at 100 °C and low oxygen pressure, 2 atm, with a substrate/carbide ratio of 1000 (mol/mol). The catalytic activity of Mo carbide and W carbide was compared with Pt/AC and Ru/AC, typical catalysts used for liquid phase oxidation of alcohols (Figure 2). Mo and W carbides appeared active in such a reaction (conversion of 85% and 62% for Mo carbide and WC carbide, respectively, after 10 h), although they were less active than Pt/AC and Ru/AC, which reached almost full conversion after 2 h.

Considering the advantage of the significantly lower cost of metal carbides (10 times less) compared with precious metal based catalysts, this result can be considered extremely positive; however, a more detailed analysis of the catalytic results highlighted additional findings. Mo carbide presented a higher initial activity than W carbide; however, observing the reaction profile, Mo carbide seems to suffer deactivation, with a decreasing of activity around 60%. XRD spectra, in fact (Figure 1), shows the structure of Mo and W before and after reaction. In the case of W carbide, XRD spectra of the fresh catalyst revealed the presence of two phases: namely, WC and W<sub>2</sub>C, the latter one disappearing after use. Because the catalyst did not undergo deactivation, we concluded that the active phase most probably was represented by WC.

By comparing fresh and used catalyst, it was evident that Mo carbide changed during the reaction with the formation of Mo–O complexes, which probably could be responsible for the deactivation observed. According to this result, we could presume that Mo<sub>2</sub>C represents the active species in this reaction and the oxygenated phase forms. By comparing the activity of Mo<sub>2</sub>C with a commercial MoO<sub>3</sub> in the same reaction, we were able to confirm this finding. In fact, MoO<sub>3</sub> showed a very low activity (Figure 1S in the Supporting Information).

Recycling reactions performed using WC, confirmed the stability of the catalyst under these reaction conditions (Figure S2 in the Supporting Information). Indeed, only a slight deactivation has been observed. Moreover the selectivity to benzyl ether and to benzaldehyde remains constant during each run.

An unexpected behavior of carbides could be outlined considering the selectivity of the reaction. Indeed, from selectivity points of view, Mo and W carbides drastically differ from supported noble metal catalysts as Pt/AC or Ru/AC (Table 2). Surprisingly, in the case of W and Mo carbides, the selectivity to benzaldehyde was reduced to 18–19%, and the

**Figure 1.** (top) XRD of WC before and after reaction. (bottom) XRD of Mo<sub>2</sub>C before and after reaction.**Figure 2.** Catalytic activity of Mo<sub>2</sub>C, WC, Pt/AC, and Ru/AC in the solventless benzyl alcohol oxidation.

one to toluene, only 1–2%. The selectivity for both catalysts was turned toward benzyl ether (70–72%) (Scheme 1). This product distribution suggested us that W and Mo carbide, differently from M/AC, can act as bifunctional catalysts, where

**Table 2.** Selectivity in the Solventless Benzyl Alcohol Oxidation<sup>a</sup>

catalyst	amount of catalyst (mg)	selectivity at 60% conversion				
		toluene	benzaldehyde	benzoic acid	benzyl benzoate	benzyl ether
W carbide	18	2	19	4	5	70
Mo carbide	19	1	18	3	6	72
Pt/AC	360 (5 wt % Pt)	15	70	3	11	1
Ru/AC	184 (5 wt % Ru)	12	74	7	7	0

<sup>a</sup>Reaction conditions: solventless; alcohol (10 g)/metal, 1000/1; T = 100 °C; pO<sub>2</sub> = 2 atm.

Table 3. Effect of reaction temperature<sup>a</sup>

catalyst	temp (°C)	time to achieve 60% conversion (h)	selectivity at 60% conversion				
			toluene	benzaldehyde	benzoic acid	benzyl benzoate	benzyl ether
W carbide	100	10	2	19	4	5	70
Mo carbide	100	2	1	18	3	6	72
W carbide	80	18	2	26	4	9	59
Mo carbide	80	14	1	30	4	6	59
W carbide	60	24	1	36	7	11	45
Mo carbide	60	24	1	39	8	4	48

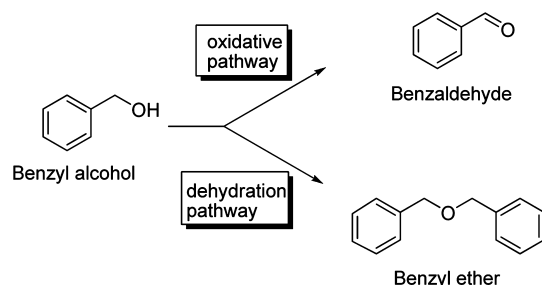
<sup>a</sup>Reaction conditions: solventless; alcohol (10 g)/metal, 1000/1; pO<sub>2</sub> = 2 atm.

Table 4. Effect of Solvent<sup>a</sup>

catalyst	time to achieve 60% conversion (h)	amount of catalyst (mg)	selectivity at 60% conversion				
			toluene	benzaldehyde	benzoic acid	benzyl benzoate	benzyl ether
W carbide	14	5		90	4	6	
Mo carbide	12	5	1	93	3	3	
Pt/AC	0.5	90 (5 wt % Pt)	4	90	2	4	
Ru/AC	0.5	46 (5 wt % Ru)	2	89	5	4	

<sup>a</sup>Reaction conditions: alcohol (2.50 g)/cyclohexane (5.85 g), 25/75 (v/v); alcohol/metal, 1000/1; T = 100 °C; pO<sub>2</sub> = 2 atm.

Scheme 1. Oxidative and Dehydration Pathways in Benzyl Alcohol Oxidation



the known acidity of these carbides (Table 1) can play an important role. Indeed, benzyl ether formation was also formed during the polymerization of benzyl alcohol using tungsten isopropoxide.<sup>17</sup> In that case, W<sub>18</sub>O<sub>49</sub> formed in situ has been recognized to catalyze the dehydration of benzyl alcohol to the corresponding diether, which can be isolated if the reaction temperature is maintained <100 °C. Also in that case, solventless conditions have been used.

The first attempt to favor the oxidative pathway was made acting on the reaction temperature (Table 3). The reaction profiles have been reported in Figure S3 of the Supporting Information. As expected, we were able to decrease the ether formation (dehydration pathway, Scheme 1) operating at 60 °C (selectivity to benzaldehyde, 39%; ether, 48%), instead of 100 °C (selectivity to benzaldehyde, 18%; ether, 72%).

Therefore, to minimize the acidic properties of the carbides, the reaction was carried out in an apolar solvent, such as cyclohexane (Table 4). The reaction profiles have been reported in Figure S4 of the Supporting Information. A drastic change in the selectivity was observed, even maintaining the T at 100 °C. Using cyclohexane at 100 °C, the production of benzyl ether was, indeed, completely avoided, and 90–93% selectivity to benzaldehyde was reached. Under the same conditions, Pt and Ru/AC showed a selectivity to benzaldehyde of 90%.

Therefore, we could conclude that with an appropriate selection of the experimental conditions, W carbide can be

considered a valid alternative to the more expensive Pt- or Ru-based catalysts. W showed good stability during the reaction, whereas a change in the Mo<sub>2</sub>C carbide structure has been observed with the formation of less active Mo–O species. The bifunctional nature of these catalysts was revealed, leading to dehydrogenation as well as dehydration products.

The relative ratio of dehydrogenation and dehydration pathways can be tuned by a careful choice of the reaction conditions.

Under solventless conditions, dehydration prevails, and a 70% selectivity to ether was obtained, whereas a >90% selectivity to benzaldehyde, a dehydrogenation product, was reached with the use of an apolar solvent.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details, catalytic activity of Mo<sub>2</sub>C vs MoO<sub>3</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [Laura.Prati@unimi.it](mailto:Laura.Prati@unimi.it), [Alberto.Villa@unimi.it](mailto:Alberto.Villa@unimi.it).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Fondazione Cariplo and Max Planck Society are gratefully acknowledge for their financial support.

## ■ REFERENCES

- (1) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037.
- (2) Besson, M.; Gallezot, P. *Catal. Today* **2000**, *57*, 127.
- (3) Sheldon, A.; Arends, I. W. C. E.; ten Brink, G. J.; Dijkstra, A. *Acc. Chem. Res.* **2002**, *35*, 774.
- (4) Bohm, H. *Nature* **1970**, *227* (5257), 483.
- (5) Lemaitre, J.; Vidick, B.; Delmon, B. *J. Catal.* **1986**, *99* (2), 415.
- (6) Levy, R. B.; Boudart, M. *Science* **1973**, *181*, 547.
- (7) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic Press: New York, 1971.

- (8) Oyama, S. T. *The Chemistry of Transition Metal Carbides and Nitrides*; Blackie Academic & Professional: London, 1996.
- (9) Xiao, T. C.; Hanif, A.; York, A. P. E.; Nishizaka, Y.; Green, M. L. *H. Phys. Chem. Chem. Phys.* **2002**, *4*, 4549.
- (10) Kojima, R.; Aika, K. *Appl. Catal., A* **2001**, *219*, 141.
- (11) Solymosi, F.; Cserenyi, J.; Szoke, A.; Bansagi, T.; Oszko, A. *J. Catal.* **1997**, *165*, 150.
- (12) Sajkowski, D. J.; Oyama, S. T. *Appl. Catal., A* **1996**, *134*, 339.
- (13) Deno, H.; Kamemoto, T.; Nemoto, S.; Koshio, A.; Kokai, F. *Appl. Surf. Sci.* **2008**, *254*, 2776.
- (14) Buha, J.; Djerdj, I.; Antonietti, M.; Niederberger, M. *Chem. Mater.* **2007**, *19*, 3499.
- (15) Gole, J. L.; Stout, J. D.; Burda, C.; Lou, Y. B.; Chen, X. B. *J. Phys. Chem. B* **2004**, *108*, 1230.
- (16) Giordano, C.; Erpen, C.; Yao, W.; Antonietti, M. *Nano Lett.* **2008**, *8* (12), 4659.
- (17) Olliges-Stadler, I.; Rossel, M.; Niederberger, M. *Small* **2010**, *6* (8), 960.