DOI: 10.1002/cctc.201300547

# A Highly Active Ni/ZSM-5 Catalyst for Complete Hydrogenation of Polymethylbenzenes

Shi-Chao Qi,<sup>[a]</sup> Xian-Yong Wei,<sup>\*[a]</sup> Zhi-Min Zong,<sup>[a]</sup> Jun-ichiro Hayashi,<sup>[b]</sup> Xin-Hua Yuan,<sup>[c]</sup> and Lin-Bing Sun<sup>[d]</sup>

Highly active supported nickel catalysts (SNCs) play crucial roles in many chemical processes, such as olefin hydrogenation,<sup>[1]</sup> cross-coupling reaction,<sup>[2]</sup> stereoselective synthesis,<sup>[3]</sup> electrochemistry,<sup>[4]</sup> and biochemistry.<sup>[5]</sup> Catalytic hydrogenation of arenes was considered to be the criterion for evaluating the activity of SNCs.<sup>[6]</sup> For instance, methanol-to-gasoline (MTG) is an important process of energy conversion, but it normally produces substantial amount of a heavy mixture (HM), which is rich in polymethylbenzenes (PMBs).<sup>[7-11]</sup> It is extremely difficult to hydrogenate PMBs, because increasing the number of methyl groups severely reduces both the equilibrium and rate constants of the hydrogenation.<sup>[1,6]</sup> Conventional methods of catalyst preparation, such as impregnation, co-precipitation, sol-gel, and in situ reduction,<sup>[12-15]</sup> are relatively tedious and no reports have been issued on the hydrogenation of PMBs with 4-6 methyl groups. Metal carbonyls (MCs) can be decomposed to fine metal particles at elevated temperatures and are thereby ideal precursors of highly active metal particles,<sup>[16]</sup> e.g., Ni-Cu surface alloys were prepared by decomposing nickel tetracarbonyl (NTC) on a copper substrate at 302 °C.<sup>[17]</sup> Although some attempts for preparing metallic catalysts using MCs have been tried since 1980s,<sup>[18-21]</sup> the preparation of SNCs, which are active enough to catalyze the hydrogenation of PMBs with 4-6 methyl groups, has not been successful, most likely because the boiling point (43 °C) of NTC is much lower than its decomposition temperature and there is a decomposition-combination equilibrium (DCE) between NTC and its decomposition products Ni and CO in a closed reactor.

[a]	SC. Qi, Prof. XY. Wei, Prof. ZM. Zong
	Key Laboratory of Coal Processing and
	Efficient Utilization (Ministry of Education)
	China University of Mining & Technology
	Xuzhou 221116 (P.R. China)
	Fax: (+86)516-83884399
	E-mail: wei_xianyong@163.com
[b]	Prof. Ji. Hayashi
	Division of Advanced Device Material
	Institute for Materials Chemistry and Engineering
	Kyushu University
	6-1, Kasuga Koen, Kasuga, Fukuoka 816-8580 (Japan)
[c]	Prof. XH. Yuan
	Materials Institute
	Jiangsu University
	Zhenjiang 212013 (P.R. China)
[d]	Prof. LB. Sun
	State Key Laboratory of Materials-Oriented Chemical Engineering
	Nanjing University of Technology
	Nanjing 210009 (P.R. China)
	Supporting information for this article is available on the WWW under
	http://dx.doi.org/10.1002/cctc.201300547.

WILEY © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Herein we report a new strategy for in situ preparation of highly active SNCs by decomposing NTC at  $100^{\circ}$ C to highly dispersive Ni onto ZSM-5. The decomposition was successively conducted to destroy the DCE by releasing the resulting CO. This strategy allows successful preparation of a highly active SNC (i.e., Ni/ZSM-5), which exhibits dramatically high activity for the hydrogenation of benzene, toluene, durene, and HM from MTG. The operating conditions of the catalyst characterizations are detailed in the Supporting Information.

As Figure 1 displays, a number of spherical particles with diameter less than 100 nm adhere to the surface of ZSM-5. The



Figure 1. SEM image of Ni/ZSM-5.

existence of Ni, Si, Al, and O in the catalyst was confirmed from EDS spectrum analysis (Figure S1). In Figure S1, a small peak area of Ni indicates a relative low Ni load, which is approximately 6.2 wt% according to ICP-OES analysis (Table 1). In Table 1, the Al content comes from the framework of ZSM-5 and the other metallic elements, except Ni, are probably due to impurities in the parent zeolite.

As shown in Figure 2, the average diameter of Ni clusters supported on ZSM-5 is smaller than 100 nm, which corresponds to the result given in Figure 1. Furthermore, in the scope of HREM, most of Ni supported onto ZSM-5 does not

Table 1. Met	Table 1. Metallic element contents in the catalyst.				
Element	Content [ppmw]	Element	Content [ppmw]		
AI	137 200.0	Cr	218.4		
Ni	62 350.0	Mn	76.2		
Fe	1695.0	Zn	70.9		
Ca	745.4	Cu	9.7		



### CHEMCATCHEM COMMUNICATIONS



Figure 2. HREM image of Ni/ZSM-5.

show the shape of crystals, but equably and amorphously disperses onto ZSM-5, which probably results from NTC decomposition at the relative low temperature. The selected area electron diffraction of Ni/ZSM-5 shows a diffraction pattern of amorphous state as well.

The characteristic diffraction peaks of Ni crystalloid at 44.5, 51.7, and 76.4° from Ni/ZSM-5 are very weak (Figure 3), suggesting the poor crystallinity of Ni on Ni/ZSM-5,<sup>[22,23]</sup> which is



Figure 3. XRD pattern of Ni/ZSM-5.

in agreement with the highly dispersive Ni on Ni/ZSM-5 as shown in Figure 1 and with the amorphous state of supported Ni, as exhibited in Figure 2.

The peaks in the profile (Figure 4) of  $H_2$  temperature-programmed reduction (TPR) located at 169.5, 301.3, and 532.5 °C



Figure 4. H<sub>2</sub> TPR profile of Ni/ZSM-5 (HC denotes H<sub>2</sub> consumption).

are attributed to the superficial reduction of NiO outside ZSM-5, the further reduction of the bulk phase NiO supported on the surface of ZSM-5, and the reduction of stabilized Ni<sup>2+</sup> species via the interaction with ZSM-5, respectively.<sup>[24]</sup> The Ni clusters could contact the support intimately, owing to their amorphously dispersive status onto ZSM-5 as shown in Figure 2.

Two broad peaks are observed in the profile of  $NH_3$  temperature-programmed desorption (TPD) for Ni/ZSM-5 (Figure 5) around 209.6 to 493.5 °C, indicating the presence of weakly and strongly acidic sites on Ni/ZSM-5, respectively. Compared



Figure 5.  $\rm NH_3$  TPD profiles of ZSM-5 and Ni/ZSM-5 (AD denotes  $\rm NH_3$  desorption).

with Ni/ZSM-5, ZSM-5 itself displays a much stronger desorption peak at 160 °C and a much weaker peak at 480 °C. These facts indicate that the amount of weak acidic sites on ZSM-5 was greatly reduced during the catalyst preparation, owing to the interaction of supported nickel with the acidic sites on ZSM-5. More strongly acidic sites, created after supporting Ni, are, however, tentatively attributed to the creation of the stronger acidic [Ni(OH)]<sup>+</sup> groups.<sup>[25]</sup>

As shown in Figure S2 and Table S1, the atomic density of Ni is approximately 2.68% on the surface of the catalyst, which further indicates a relative low Ni load. In Figure 6, the multi-



Figure 6. XPS spectrum of Ni 2p<sub>3/2</sub> region after deconvolution for Ni/ZSM-5.

peaks located at 852.2, 852.8, and 853.6 eV denote the chemical bonds of metallic Ni, Ni<sub>2</sub>Si, and Al<sub>3</sub>Ni, respectively.<sup>[26–28]</sup> Main peak located at 856.4 eV demonstrates the existence of  $[Ni(OH)]^{+}$ .<sup>[29]</sup> The  $E_{B}$  of the satellite peak for NiO is characteristic at 861.5 eV.<sup>[30]</sup> These facts indicate that supported Ni partially interacts with ZSM-5, especially with the acidic sites of ZSM-5, which is in agreement with the reduction of acidic sites of ZSM-5 in Figure 5.

As Figure 7 illustrates, the isotherms are classical type-IV isotherms with little uptakes at high partial pressures.<sup>[31]</sup> Each of the isotherms has a typical type-H4 hysteresis loop, indicating the presence of mesopores both in ZSM-5 and in Ni/ZSM-5.<sup>[31]</sup> The specific surface area of ZSM-5 falls down from 270 m<sup>2</sup>g<sup>-1</sup> to 185 m<sup>2</sup>g<sup>-1</sup> after supporting Ni. The microporosity of Ni/ZSM-5 is not noticeably different from that of ZSM-5, and the mesoporous are only partially blocked. These facts indicate that most of the NTC decomposed on the surface of ZSM-5, while only a small amount of the NTC was impregnated into the mesopores of ZSM-5 and then decomposed there.

Benzene is most inert toward hydrogenation in non-substituted arenes and the substitution of methyl group further de-

<sup>© 2013</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 7. A)  $\mathsf{N}_2$  adsorption/desorption isotherms and B) pore-size distribution of ZSM-5 and Ni/ZSM-5.

creases the reactivity of benzene ring toward hydrogenation due to steric effects.<sup>[32–34]</sup> The decrease is significant by comparing catalytic hydrogenation of benzene with that of toluene over Ni/ZSM-5 under the same conditions (Figure S3). It can be imaged that the hydrogenation of PMBs should be more difficult. However, neither benzene nor toluene is well hydrogenated over the Ni/ZSM-5-C prepared via conventional impregnation and drying, indicating a higher catalytic efficiency of Ni/ ZSM-5 than Ni/ZSM-5-C (Figure S3). The kinetics of durene hydrogenation was investigated over Ni/ZSM-5 in the temperature range of 100–220 °C. As shown in Figure 8, neglecting the



Figure 8. Kinetics of durene hydrogenation.

impact on the reaction order from temperatures and catalyst deactivation, good linear relations between durene conversion X and the reaction time t suggest a close zero-order reaction with respect to durene, which corresponds to previous reports on PMBs hydrogenation.<sup>[34,35]</sup> The relation between X and t can be expressed as: X = kt, where k denotes the close zero-order rate constant.

The rate constants are calculated from the slopes of plots of *X* versus *t* for each reaction temperature and listed in Table 2. Based on data in Table 2, an Arrhenius plot was obtained (Figure 9), which also shows a good linear correlation. The apparent activation energy ( $E_a$ ) estimated from the slope of  $\ln k$  versus  $T^{-1}$  plot is only 12.2 kJ mol<sup>-1</sup>, which is much lower than previous reports on the  $E_a$  (40-60 kJ mol<sup>-1</sup>) of arene hydrogenation over nickel catalysts.<sup>[35-37]</sup> 1,2,4,5-Tetramethylcyclohexane is the only product from durene hydrogenation (Figure S4). Indeed, the hydrogenation of durene was also performed over Ni/ZSM-5-C, but there was no saturated product detected in

Table 2. Close zero-order reaction rate constants for durene hydrogenation.					
<i>т</i> [°С]	<i>k</i> [·10 <sup>-2</sup> h <sup>-1</sup> ]	<i>T</i> [°C]	<i>k</i> [·10 <sup>-2</sup> h <sup>-1</sup> ]		
100 130 160	4.33 5.78 7.21	190 220	9.07 11.42		



Figure 9. Arrhenius plots for durene hydrogenation.

a wide reaction temperature range of 100-220 °C, which further demonstrates the superior efficiency of Ni/ZSM-5, especially for the hydrogenation of PMBs.

As shown in Figure S5 and Table S2, main components in HM are arenes, especially PMBs. The PMBs are extremely difficult to be saturated; meanwhile the blended arenes would restrain mutual reactivity toward hydrogenation, owing to the competitive adsorption on the catalyst used.[38-41] The high activity of Ni/ZSM-5 toward hydrogenation successfully overcomes the difficulties. As Figure S5 and Table S3 (HHM denotes hydrogenated HM) exhibit, all the arenes in HM were catalytically hydrogenated to saturated species over Ni/ZSM-5 at 180 °C for 20 h. Such outstanding catalytic activity of Ni/ZSM-5 is attributed to the following two reasons: the amorphous state of Ni supported on ZSM-5 and the strong interaction between Ni and the support. The amorphous dispersion of Ni significantly enhances the opportunity of interaction between substrates and the catalyst; meanwhile, the synergic effect between Ni and acidic support creates an electron-deficient surface, which substantially increases the activity of Ni loaded and facilitates the activation of the  $\pi$  bond in the arenes.  $^{[42-46]}$ 

The stability of Ni/ZSM-5 was examined according to catalytic hydrogenation of durene at 180 °C for 10 h using fresh and used Ni/ZSM-5. As Figure 10 displays, durene conversion *X* decreases with increasing recycle number of the catalyst and drops to approximately 20% after the 3rd recycle. Analysis of the HREM image of the recycled catalyst in Figure 10 reveals the severe agglomeration of nickel clusters over ZSM-5, caused by the long catalytic reaction time at 180 °C, which is regarded as the main reason for catalyst deactivation.

In summary, using NTC as the precursor, a highly dispersive and active Ni/ZSM-5 catalyst was prepared by successively releasing the resulting CO. Nickel amorphously disperses onto ZSM-5 and strongly interacts with the support. The catalyst shows very high activity for the hydrogenation of benzene, tol-

<sup>© 2013</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 10. Test of the Ni/ZSM-5 (left, RN denotes recycle number) and HREM image of Ni/ZSM-5 after 3-times of recycle (right).

uene, durene, and a series of PMBs in HM from MTG. Especially, complete hydrogenation of all the arenes in the HM was achieved over the catalyst. This strategy may open up a route for the design and preparation of more active supported metal catalysts.

#### **Experimental Section**

NTC was synthesized by the reaction of active Ni powder with CO under 8.0 MPa at 100 °C in a 100 mL stainless steel and magnetically stirred autoclave. Diethyl ether (25 mL), ZSM-5 (8 g, particle size < 178  $\mu$ m), and NTC (2 mL) were put into the autoclave. After replacing air inside the autoclave with N<sub>2</sub>, the mixture in the autoclave was slowly stirred (70 rpm) for 1 h at room temperature to sufficiently impregnate NTC onto ZSM-5. Then the autoclave was heated to 100°C and kept at the temperature for 1 h with rapid agitation (150 rpm) to allow in situ decomposition of NTC onto ZSM-5. After cooling the autoclave, CO in the autoclave was released followed by subsequent heating and cooling mentioned above to decompose NTC as exhaustively as possible. Then the reaction mixture was taken out from the autoclave and filtrated under N<sub>2</sub> protection to obtain the supported Ni catalyst (i.e. Ni/ ZSM-5), in which the Ni loaded was measured by using a ICP-OES Agilent 720. The catalyst was characterized by using a Hitachi S-3700N scanning electron microscope (SEM) combined with an energy dispersive spectrometer (EDS), JEOL JEM-2100 high resolution electronic microscope (HREM), Bruker Advance X-ray diffractometer (XRD), TP-5080 automatic adsorption apparatus for H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD, Thermo Escalab 250XI apparatus for XPS measurement and Autosorb-1 MP apparatus for N<sub>2</sub> adsorption-desorption. The comparative same Ni loaded catalyst was prepared by impregnating ZSM-5 (8 g) with an aqueous solution containing Ni-(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (9 mmol) under stirring at 60°C until dryness, and drying at 100 °C overnight. The dried sample was calcined at 550 °C for 4 h under air to obtain NiO/ZSM-5, followed by reduced at 550 °C in H<sub>2</sub> flow of 30 mLmin<sup>-1</sup> for 4 h to obtain the catalyst (marked Ni/ZSM-5-C).<sup>[47]</sup>

Solvent cyclohexane or tetrahydrofuran (only for the substrate benzene) (20 mL), catalyst (0.5 g) and a substrate (arene 5 mmol or HM 1.0 g) were fed into the autoclave. After replacing air in the autoclave and being pressurized with hydrogen to 5.0 MPa at room temperature, the autoclave was heated up to an indicated temperature within 20 min and kept at the temperature for a prescribed period of time with rapid agitation (250 rpm), and the total pressure inside the autoclave was maintained higher than 6.0 MPa via www.chemcatchem.org

timely  $H_2$  supplement during indicated temperature heating. The reaction mixture was taken out from the autoclave and filtrated after cooling the autoclave in a water bath. The filtrate was analyzed by using a Hewlett–Packard 6890/ 5973 gas chromatograph/mass spectrometer.

#### Acknowledgements

This work was supported by National Basic Research Program of China (Grant 2011CB201302), Na-

tional Natural Science Foundation of China (Grants 20936007, 51221462, and 51074153), the Key Project of Coal Joint Fund from National Natural Science Foundation of China and Shenhua Group Corporation Limited (Grant 51134021), Strategic Chinese-Japanese Joint Research Program (Grant 2013DFG60060), the Fundamental Research Fund for the Doctoral Program of Higher Education (Grant 20120095110006) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

**Keywords:** amorphous • hydrogenation • nickel polymethylbenzene • porous materials

- [1] A. Stanislaus, B. H. Cooper, Catal. Rev. 1994, 36, 75-123.
- [2] K. Tamao, J. Organomet. Chem. 2002, 653, 23-26.
- [3] M. Takimoto, Y. Hiraga, Y. Sato, M. Mori, *Tetrahedron Lett.* 1998, 39, 4543-4546.
- [4] K. Urgin, R. Barhdadi, S. Condon, E. Léonel, M. Pipelier, V. Blot, C. Thobie-Gautier, D. Dubreuil, *Electrochim. Acta* 2010, 55, 4495–4500.
- [5] P. Mullai, M. K. Yogeswari, K. Sridevi, Bioresour. Technol. 2013, DOI: 10.1016/j.biortech.2013.03.082.
- [6] B. H. Cooper, B. Donnis, Appl. Catal. A 1996, 137, 203-223.
- [7] A. G. Gayubo, P. L. Benito, A. T. Aguayo, Chem. Eng. Sci. 1996, 51, 3001– 3006.
- [8] A. T. Aguayo, A. G. Gayubo, J. Ortega, Catal. Today 1997, 37, 239-248.
- [9] M. Bjorgen, S. Svelle, F. Joensen, J. Nerlov, S. Kolboe, F. Bonino, L. Palumbo, S. Bordiga, U. Olsbye, J. Catal. 2007, 249, 195–207.
- [10] M. Bjørgen, F. Joensen, M. S. Holm, U. Olsbye, K. P. Lillerud, S. Svelle, *Appl. Catal. A* 2008, 345, 43-50.
- [11] F. L. Bleken, T. V. W. Janssens, S. Svelle, U. Olsbye, Microporous Mesoporous Mater. 2012, 164, 190-198.
- [12] K. Y. Tsai, I. Wang, T. C. Tsai, Catal. Today 2011, 166, 73-78.
- [13] Z. Guo, W. Huo, M. Jia, J. Mol. Catal. A 2010, 326, 82-87.
- [14] P. G. Savva, K. Goundani, J. Vakros, Appl. Catal. B 2008, 79, 199-207.
- [15] A. G. Boudjahem, W. Bouderbala, M. Bettahar, *Fuel Process. Technol.* **2011**, *92*, 500–506.
- [16] K. S. Suslick, J. W. Goodale, P. F. Schubert, J. Am. Chem. Soc. 1983, 105, 5781–5785.
- [17] P. F. A. Alkemade, H. Fortuin, R. Balkenende, F. H. P. M. Habraken, W. F. van der Weg, Surf. Sci. 1990, 225, 307–318.
- [18] A. Brenner, D. A. Hucul, J. Catal. 1980, 61, 216-222.
- [19] A. Brenner, D. A. Hucul, S. Hardwick, J. Inorg. Chem. 1979, 18, 1478– 1484.
- [20] D. Mahajan, E. T. Papish, K. Pandya, Ultrason. Sonochem. 2004, 11, 385– 392.
- [21] E. Redel, J. Krämer, R. Thomann, J. Organomet. Chem. 2009, 694, 1069– 1075.
- [22] A. Masalska, Appl. Catal. A 2005, 294, 260-272.
- [23] J. M. Rynkowski, T. Paryjczak, M. Lennik, Appl. Catal. A 1993, 106, 73-82.
- [24] M. A. Ermakova, D. Y. Ermakov, Appl. Catal. A 2003, 245, 277-288.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

ChemCatChem 0000, 00, 1-5

## CHEMCATCHEM COMMUNICATIONS

- [25] B. I. Mosqueda-Jiménez, A. Jentys, K. Seshan, J. A. Lercher, J. Catal. 2003, 218, 348–353.
- [26] R. P. Furstenau, G. McDougall, M. A. Langell, Surf. Sci. 1985, 150, 55-79.
- [27] P. J. Grunthaner, F. J. Grunthaner, J. W. Mayer, J. Vac. Sci. Technol. 1980, 17, 924–929.
- [28] F. U. Hillebrecht, J. C. Fuggle, P. A. Bennett, Z. Zolnierek, *Phys. Rev. B* 1983, 27, 2179-2193.
- [29] K. S. Kim, N. Winograd, Surf. Sci. 1974, 43, 625-643.
- [30] A. N. Mansour, Surf. Sci. Spectra 1994, 3, 231-238.
- [31] D. S. Kim, S. M. Kim, J. S. Chang, S. E. Park, Stud. Surf. Sci. Catal. 2001, 135, 333.
- [32] M. C. Tsai, E. L. Muetterties, J. Am. Chem. Soc. 1982, 104, 2534-2539.
- [33] V. Meille, E. Schulz, M. Lemaire, J. Catal. 1997, 170, 29-36.
- [34] P. Michaud, J. L. Lemberton, G. Pérot, *Appl. Catal. A* **1998**, *169*, 343–353.
- [35] A. K. Neyestanaki, H. Backman, P. Mäki-Arvela, J. Wärna, T. Salmi, D. Y. Murzin, Chem. Eng. J. 2003, 91, 271–278.
- [36] S. Smeds, T. Salmi, D. Y. Murzin, Appl. Catal. A 1999, 185, 131-136.
- [37] J. W. Thybaut, M. Saeys, G. B. Marin, Chem. Eng. J. 2002, 90, 117-129.

- [38] J. Wang, H. Chen, Q. Li, React. Kinet. Catal. Lett. 2000, 69, 277-284.
- [39] T. C. Huang, B. C. Kang, Ind. Eng. Chem. Res. 1995, 34, 1140-1148.
- [40] K. Ito, Y. Kogasaka, H. Kurokawa, Fuel Process. Technol. 2002, 79, 77-80.
- [41] S. Jongpatiwut, Z. Li, D. E. Resasco, *Appl. Catal. A* 2004, *262*, 241–253.
  [42] X. Y. Wei, Z. H. Ni, Z. M. Zong, S. L. Zhou, Y. C. Xiong, X. H. Wang, *Energy Fuels* 2003, *17*, 652–657.
- [43] L. B. Sun, Z. M. Zong, J. H. Kou, L. F. Zhang, Z. H. Ni, G. Y. Yu, H. Chen, X. Y. Wei, C. W. Lee, *Energy Fuels* **2004**, *18*, 1500–1504.
- [44] M. Koussathana, D. Vamvouka, M. Tsapatsis, *Appl. Catal. A* **1992**, *80*, 99–113.
- [45] J. Wang, L. Huang, Q. Li, Appl. Catal. A 1998, 175, 191–199.
- [46] M. Ziolek, J. Nowak, C. Lavalley, Catal. Lett. 1997, 45, 259-265.
- [47] S. B. Ren, P. Zhang, H. F. Shui, Catal. Commun. 2010, 12, 132–136.

Received: July 9, 2013 Published online on ■■ ■, 0000

# COMMUNICATIONS

S.-C. Qi, X.-Y. Wei,\* Z.-M. Zong, J.-i. Hayashi, X.-H. Yuan, L.-B. Sun

#### 

A Highly Active Ni/ZSM-5 Catalyst for Complete Hydrogenation of Polymethylbenzenes



Amazing the crowd: A highly dispersive supported nickel catalyst is prepared by in situ decomposition of Ni(CO)<sub>4</sub> over ZSM-5 zeolite. The catalyst displays an amazing activity for complete hydrogenation of polymethylbenzenes which are extremely difficult to be saturated.