



Article

# Turnover Rate of Metal-Catalyzed Hydroconversion of 2,5-Dimethylfuran: Gas-Phase Versus Liquid-Phase

Hanan Althikrallah <sup>1,2</sup>, Casper Kunstmann-Olsen <sup>1</sup> , Elena F. Kozhevnikova <sup>1</sup> and Ivan V. Kozhevnikov <sup>1,\*</sup> 

<sup>1</sup> Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK; pshalhi@liverpool.ac.uk (H.A.); casper.kunstmann@york.ac.uk (C.K.-O.); efkozhev@liverpool.ac.uk (E.F.K.)

<sup>2</sup> Department of Chemistry, College of Science, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia

\* Correspondence: kozhev@liverpool.ac.uk; Tel.: +44-151-794-2938

Received: 17 September 2020; Accepted: 7 October 2020; Published: 12 October 2020



**Abstract:** Hydroconversion (hydrogenation and hydrogenolysis) of biomass-derived furanic compounds giving furan ring-hydrogenation and ring-cleavage products attracts interest for sustainable production of chemicals and fuels. Here, the hydroconversion of 2,5-dimethylfuran (DMF), chosen as a model furanic compound, was investigated at a gas-solid interface over carbon-supported Pt, Pd, Rh and Ru metal catalysts in a fixed-bed reactor at 70–90 °C and ambient pressure. Pt/C was mainly active in ring cleavage of DMF to produce 2-hexanone as the primary product, followed by its hydrogenation to 2-hexanol and hexane. In contrast, Pd/C, Rh/C and Ru/C selectively hydrogenated the furan ring to 2,5-dimethyltetrahydrofuran (DMTHF). The turnover frequency (TOF) of metal sites in the gas-phase DMF hydroconversion was determined from zero-order kinetics in the absence of diffusion limitations. The TOF values decreased in the sequence Pt > Rh > Pd >> Ru, similar to the liquid-phase reaction. The TOF values for the gas-phase reaction were found to be one order of magnitude greater than those for the liquid-phase reaction. This indicates that the gas-phase process is potentially more efficient than the liquid-phase process. TOF values for hydroconversion of ring-saturated furan derivatives, tetrahydrofuran and DMTHF, on Pt/C, were much lower than those for DMF.

**Keywords:** 2,5-dimethylfuran; hydrogenation; hydrogenolysis; noble metal catalysts; turnover frequency

## 1. Introduction

Furanic compounds derived from biomass attract considerable interest as a renewable feedstock, which can be converted to transportation fuels, lubricants and a wide range of value-added chemicals such as aldehydes, ketones and alcohols via catalytic hydrogenation, hydrogenolysis and hydrodeoxygenation, hereinafter referred to as hydroconversion ([1–14] and references therein). These reactions can be carried out over supported metal catalysts in gas or liquid phase. It has been reported that in hydrogenation of furanic compounds, such as 2-methylfuran, 2,5-dimethylfuran (DMF) and furfural, Pt exhibits a higher selectivity to ring-opened products (ketones and alcohols), whereas Pd, Rh and Ru have high selectivity to ring-saturated tetrahydrofuran derivatives ([6,8,13] and references therein). The difference in selectivity of Pt from Pd, Rh and Ru has been explained by different bonding of furanic compounds to these metals [6,15]. According to a density functional theory (DFT) study [15], furan ring binds parallel to noble metal surface either via a single  $\pi$  C=C bond or via two  $\sigma$  bonds with two C atoms of the C=C bond. The  $\sigma$ -bonding is preferred for Pt, whereas the  $\pi$ -bonded mode is favourable for Pd, Rh and Ru. It is suggested that  $\sigma$ -bonding, distorting the aromaticity of the furan

ring, favours ring hydrogenolysis, whereas  $\pi$ -bonding favours ring hydrogenation [6,15]. Nevertheless, initial  $\pi$ -bonding of DMF to a Pt site may play an important role in this reaction (see Section 2.3 below).

Platinum, due to its high activity in hydrogenolysis of furan rings, is one of the most efficient catalysts for hydroconversion of furanic compounds to ring-opened products. It has been demonstrated that in hydroconversion of DMF on Pt, 2-hexanone, the primary ring-opened product, and 2,5-dimethyltetrahydrofuran (DMTHF), the primary ring-saturated product, are formed directly from DMF in parallel pathways [6,13]. Ring cleavage of DMF has been reported to be 14 times faster than ring saturation on 5%Pt/C in the liquid-phase batch reaction (in nonane, 80 °C, 5.5 bar H<sub>2</sub>) [6] and 9 times faster in the gas-phase flow reaction on 1% Pt/h-BN (hexagonal boron nitride support, 200 °C, 1 bar H<sub>2</sub>) [13].

The gas-phase hydroconversion process can be expected to be more efficient and environmentally benign than the liquid-phase process due to low hydrogen pressure, continuous operation and easy product separation. In this connection, it is interesting to compare catalyst turnover rates for the gas-phase and liquid-phase hydroconversion of furanic compounds. Turnover rate or turnover frequency (TOF) is the rate of reaction referred to the number of catalytic sites. It provides information about the rate at which catalytic cycles turn over, which is useful both for theory and practice of catalysis [16].

Recently, Louie et al. [6] have reported a detailed kinetic study of liquid-phase DMF hydroconversion in a batch reactor over commercial carbon-supported Pt, Pd, Rh and Ru catalysts (5–10% nominal metal loading) and provided the TOF values for all the catalysts at identical conditions (80 °C, 5.5 bar H<sub>2</sub>, nonane as a solvent), with the number of surface metal sites determined from CO chemisorption.

In this work, we investigate the gas-phase hydroconversion of 2,5-dimethylfuran (DMF), chosen as a model for biomass-derived furanic compounds, in a fixed-bed flow reactor over the same commercial carbon-supported noble metal catalysts (3–10 wt% nominal metal loading) at similar conditions (70–90 °C), except at ambient pressure. The metal dispersion is measured using CO chemisorption as in [6]. The TOF values of metal sites are determined from zero-order kinetics in the absence of diffusion limitations and compared with those reported for the liquid-phase reaction [6]. It is demonstrated that the gas-phase hydroconversion of DMF over the carbon-supported noble metal catalysts is much more efficient than the corresponding liquid-phase reaction, with the TOF values one order of magnitude greater than those in the liquid phase. In addition, hydrogenolysis of ring-saturated furanic compounds, tetrahydrofuran (THF) and 2,5-dimethyltetrahydrofuran (DMTHF) are studied for comparison with DMF.

## 2. Results and Discussion

### 2.1. Gas-Phase Hydroconversion of DMF over Carbon-Supported Noble Metal Catalysts

Table 1 shows the performance of Pt, Pd, Rh and Ru carbon-supported catalysts in the gas-phase hydroconversion of DMF at 70–90 °C and relatively long contact times  $W/F = 25\text{--}125\text{ g}\cdot\text{h}\cdot\text{mol}^{-1}$ . At such conditions, all these catalysts gave ~100% DMF conversion. As expected, Pt gave mainly ring-cleavage products (2-hexanone, 2-hexanol and hexane) in 85% total selectivity together with a small amount of the ring-hydrogenation product 2,5-dimethyltetrahydrofuran (DMTHF, *cis* and *trans* isomers, 7–13% selectivity). Reaction time course with Pt/C at 90 °C for 20 h time on stream (TOS) is shown in Figure S1 (Supplementary Materials). In contrast, Pd, Rh and Ru were active in ring hydrogenation, yielding almost exclusively DMTHF, with the selectivity increasing in the order  $\text{Ru} < \text{Rh} \leq \text{Pd}$ . *cis*-DMTHF, having a lower boiling point and a shorter gas chromatography (GC) retention time [17], was the predominant isomer (*cis/trans* = 6–10).

The M/C catalysts, except Pd/C, exhibited some deactivation, which can be seen at shorter contact times. Thus, for Pt/C, the conversion of DMF at 70 °C and  $W/F = 2.5\text{ g}\cdot\text{h}\cdot\text{mol}^{-1}$  declined from 100 to 77% in 5 h TOS, while the product selectivity remained unchanged (Figure 1). At such conditions,

2-hexanone rather than 2-hexanol was the main reaction product (57% selectivity). Catalyst deactivation was not unexpected since metal catalysts usually experience deactivation in hydrogenation of C=C bonds, which is thought to be caused by carbonaceous deposits blocking active metal sites [18]. Surprisingly, Pd/C exhibited stable activity at least for 3 h TOS, as can be seen from Figure 2 at 61% DMF conversion level. Deactivation of Pt/C obeyed first order rate law (Figure S2). For the data shown in Figure 1, the deactivation rate constant was  $k_d = 8.0 \times 10^{-4} \text{ min}^{-1}$ . Spent Pt/C catalysts could be fully regenerated by treating in situ with air followed by reduction with H<sub>2</sub> (Figure S3, see the Supplementary Materials for regeneration details). The fact that the selectivity did not change while the activity decayed suggests that deactivation reduced the number of active metal sites without affecting the state of the remaining sites.

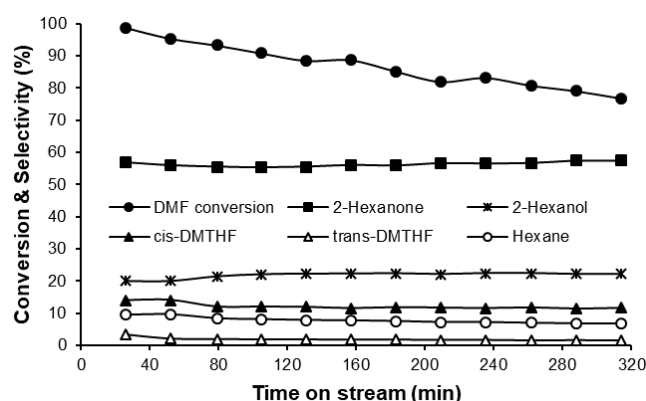
**Table 1.** Hydroconversion of 2,5-dimethylfuran over noble metal catalysts <sup>1</sup>.

Catalyst <sup>2</sup>	W/F (g·h·mol <sup>-1</sup> )	Conv. <sup>3</sup> (%)	Product Selectivity <sup>3</sup> (%)				
			Hexane	DMTHF <sup>4</sup>	2-Hexanone	2-Hexanol	Other
9.6%Pt/C + SiO <sub>2</sub> (20)	25	>99	11.6	13.1	0.9	72.5	1.9
9.6%Pt/C + SiO <sub>2</sub> (20) <sup>5</sup>	25	>99	8.8	10.7	2.1	74.2	4.2
7.0%Pt/C + SiO <sub>2</sub> (100) <sup>5,6</sup>	125	>99	19.8	7.3	4.6	61.4	6.9
7.8%Pd/C + SiO <sub>2</sub> (25)	31	>99	0.0	99.8	0.0	0.0	0.2
3.0%Ru/C + SiO <sub>2</sub> (67)	83	>99	0.0	94.6	0.0	4.7	0.6
4.0%Rh/C + SiO <sub>2</sub> (40)	50	>99	0.0	99.6	0.0	0.3	0.1

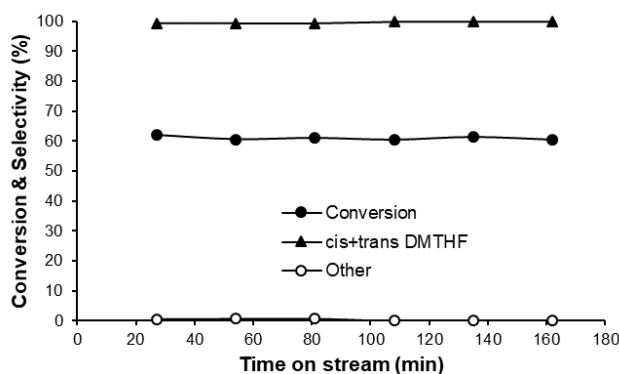
<sup>1</sup> 70 °C, 1.6 kPa DMF partial pressure, 20 mL min<sup>-1</sup> H<sub>2</sub> flow rate, 4 h TOS. <sup>2</sup> Catalyst bed a mixture of M/C + SiO<sub>2</sub> (0.20 g total weight, 1% metal loading per total catalyst weight); in round brackets the amount of M/C (mg).

<sup>3</sup> Average conversion and product selectivity over 4 h TOS. <sup>4</sup> A mixture of *cis* and *trans* isomers (*cis/trans* = 6–10).

<sup>5</sup> At 90 °C. <sup>6</sup> 3.5% Pt loading, H<sub>2</sub> + N<sub>2</sub> (1:3 v/v) gas flow (0.25 bar H<sub>2</sub> partial pressure).



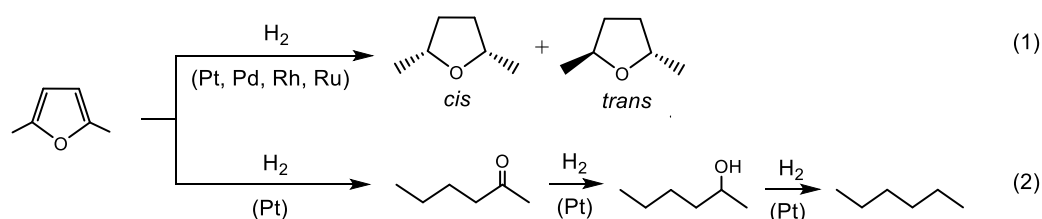
**Figure 1.** Time course for DMF hydroconversion over 7.0%Pt/C + SiO<sub>2</sub> catalyst (0.20 g total weight, 2.0 mg Pt/C) at 1.6 kPa DMF partial pressure, 70 °C, 20 mL min<sup>-1</sup> H<sub>2</sub> flow rate, W/F = 2.5 g h mol<sup>-1</sup>.



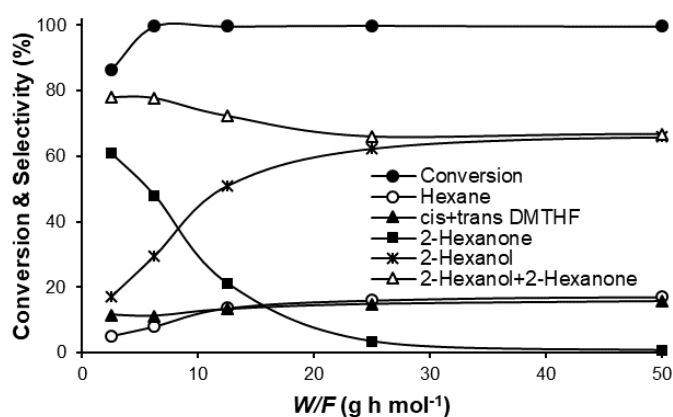
**Figure 2.** Time course for DMF hydrogenation over 7.8%Pd/C + SiO<sub>2</sub> catalyst (0.20 g total weight, 0.6 mg Pd/C) at 1.6 kPa DMF partial pressure, 70 °C, 40 mL min<sup>-1</sup> H<sub>2</sub> flow rate, W/F = 0.38 g·h·mol<sup>-1</sup>.

The results shown in Table 1 demonstrate that the selectivity pattern in the gas-phase DMF hydroconversion in a flow system is similar to that reported previously for the liquid-phase batch reaction in the presence of similar carbon-supported noble metal catalysts [6]. Importantly, the gas-phase reaction occurred more efficiently and under milder conditions than the liquid-phase one. Thus, in the gas phase, Pt/C gives ~100% DMF conversion at 70 °C and ambient pressure (Table 1), whereas in the liquid phase 80% conversion in 0.5 h at 80 °C and 5.5 bar H<sub>2</sub> pressure [6]. The liquid-phase reaction requires elevated H<sub>2</sub> pressure to overcome low H<sub>2</sub> solubility. The gas-phase reaction with Pt/C occurs with full DMF conversion even at a H<sub>2</sub> partial pressure as low as 0.25 bar (Table 1). Consequently, the gas-phase hydroconversion of DMF occurs deeper than the liquid-phase one. In the liquid-phase reaction over Pt/C, 2-hexanone has been reported to be the main product [6], whereas in the gas-phase 2-hexanone underwent further hydrogenation to give 2-hexanol (74% yield at 90 °C, Table 1).

The proposed reaction network for the metal-catalysed DMF hydroconversion in the gas phase is shown in Scheme 1. It reflects upon the different reaction selectivity of Pt, on one hand, and Pd, Rh and Ru, on the other. The parallel pathways of ring saturation (1) and ring cleavage (2) on Pt occur with a cleavage/saturation molar ratio of 6–12 (Table 1) in agreement with previous reports [6,13]. It has been suggested that the ring-cleavage pathway on Pt may proceed via initial enol formation, followed by keto-enol tautomerization [6]. Further consecutive hydrogenations lead to the formation of 2-hexanone, 2-hexanol and hexane. In liquid-phase DMF hydroconversion on Pt/C, 2-hexanol has been reported to be partly formed in parallel to 2-hexanone by direct hydrogenation of enol [6]. In our system, no such pathway was observed; our results indicate that 2-hexanol is formed by hydrogenation of 2-hexanone as shown in Scheme 1. This is supported by the plot of reaction selectivity versus the contact time  $W/F$  (Figure 3), which clearly shows that 2-hexanol is produced by hydrogenation of 2-hexanone. Therefore, the ring-cleavage pathway (2) in the gas phase is different from that in the liquid phase.



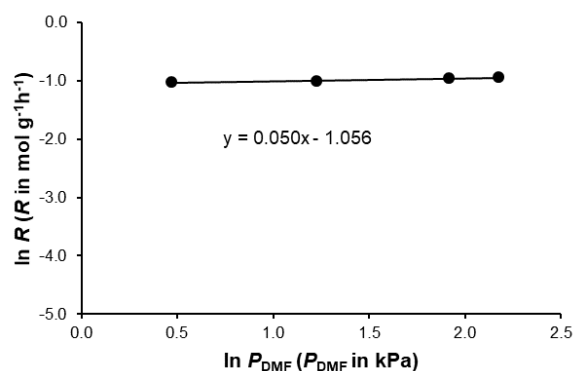
**Scheme 1.** Reaction network for hydroconversion of DMF catalysed by noble metals.



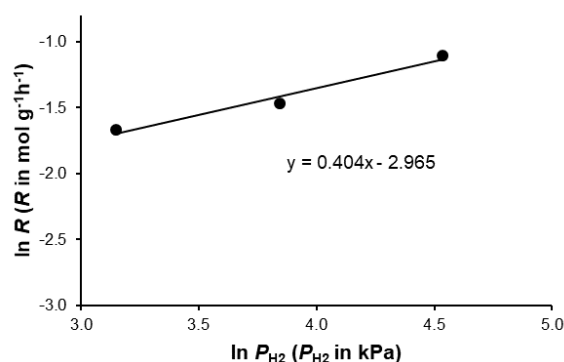
**Figure 3.** Plot of DMF conversion and product selectivity versus contact time  $W/F$  for hydroconversion of DMF (7.0%Pt/C + SiO<sub>2</sub> catalyst (0.20 g), 1.6 kPa DMF partial pressure, 70 °C, 20 mL·min<sup>-1</sup> H<sub>2</sub> flow rate, 1 h TOS; the  $W/F$  was varied by varying the amount of 7.0%Pt/C in the Pt/C + SiO<sub>2</sub> mixture).

## 2.2. Turnover Rate: Gas Phase Versus Liquid Phase

Kinetics of the gas-phase hydroconversion of DMF over M/C catalysts was examined focusing mainly on Pt/C as the most active catalyst. The reaction rates were determined at short contact times  $W/F = 0.13\text{--}1.9\text{ g}\cdot\text{h}\cdot\text{mol}^{-1}$  and 1 h TOS. At such conditions, catalyst deactivation was small (see Section 3 for details). The rate of DMF hydroconversion on Pt/C was found to be zero order in DMF partial pressure (Figure 4), which indicates that the catalyst was saturated with DMF molecules. The order in hydrogen partial pressure was found to be 0.40 (Figure 5). Zero order in DMF was also found for Pd/C, Rh/C and Ru/C. It should be noted that a zero-order reaction rate does not depend on DMF conversion and is equal to the rate constant.



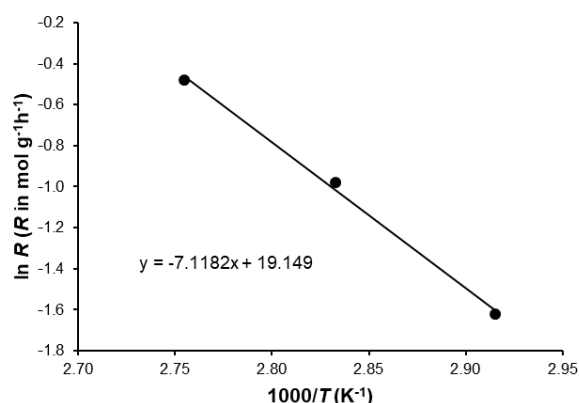
**Figure 4.** Effect of DMF partial pressure on the rate of DMF hydroconversion over 9.6%Pt/C + SiO<sub>2</sub> catalyst (0.10 g total weight, 1.3 mg Pt/C) at 70 °C, 40 mL min<sup>-1</sup> H<sub>2</sub> flow rate.



**Figure 5.** Effect of hydrogen partial pressure on the rate of DMF hydroconversion over 9.6%Pt/C + SiO<sub>2</sub> catalyst (0.20 g total weight, 2.5 mg Pt/C) at 6.8 kPa DMF partial pressure, 70 °C, 40 mL·min<sup>-1</sup> H<sub>2</sub> + N<sub>2</sub> flow rate with varied H<sub>2</sub>/N<sub>2</sub> ratio.

The reaction over Pt/C had an activation energy  $E = 59.2\text{ kJ}\cdot\text{mol}^{-1}$  (see the Arrhenius plot in Figure 6). Given zero reaction order, this is a true value of  $E$ . The high  $E$  value and zero order in DMF indicate that the reaction is not diffusion limited and occurs under kinetic control. This conclusion was further strengthened via Weisz-Prater analysis [19], which also indicated no internal diffusion limitation in this reaction (Weisz-Prater criterion estimated to be  $C_{\text{WP}} = 0.14$  at 70 °C, see Supplementary Materials for details).

The kinetic parameters found for Pt/C are similar to those reported for the liquid-phase reaction over Pt/C in nonane as a solvent:  $E_a = 45.3\text{ kJ}\cdot\text{mol}^{-1}$  (70–100 °C), zero order in DMF and 0.6 order in H<sub>2</sub> [6]. For the liquid-phase DMF hydroconversion on Pt/C, a mechanism involving non-competitive adsorption of DMF and H<sub>2</sub> on Pt sites has been suggested [6]. A similar mechanism may be expected to operate in the gas-phase hydroconversion of DMF over Pt/C.



**Figure 6.** Arrhenius plot for DMF hydroconversion over 9.6%Pt/C + SiO<sub>2</sub> catalyst (0.20 g total weight, 2.5 mg Pt/C) at 6.8 kPa DMF partial pressure, 70–90 °C, 40 mL·min<sup>-1</sup> flow rate ( $E = 59.2$  kJ·mol<sup>-1</sup>).

Table 2 presents the total turnover frequency of metal sites and product selectivity of DMF hydroconversion over M/C catalysts in the gas phase at 70 °C, 1 bar H<sub>2</sub> pressure and DMF conversion range  $X = 24$ –61%. The TOF values were calculated from zero-order reaction rates using metal dispersion given in Section 3 (Materials and Methods). Selectivity patterns at lower DMF conversion  $X = 24$ –61% (short contact times  $W/F = 0.13$ –1.88 g·h·mol<sup>-1</sup>) were similar to that at  $X = \sim 100\%$  ( $W/F = 25$ –125 g·h·mol<sup>-1</sup>) (Table 1), except for Pt/C, which gave 2-hexanone as the main product rather than 2-hexanol, as expected at shorter contact times.

**Table 2.** Turnover frequencies of noble metals in DMF hydroconversion<sup>1</sup>.

Catalyst <sup>2</sup>	W/F (g·h·mol <sup>-1</sup> )	Conv. <sup>3</sup> (%)	TOF <sup>4</sup> (s <sup>-1</sup> )	Product Selectivity <sup>3</sup> (%)				
				Hexane	DMTHF <sup>5</sup>	2-Hexanone	2-Hexanol	Other
9.6%Pt/C (1.0)	0.63	24.2	5.6	3.3	12.9	61.3	20.8	1.7
9.6%Pt/C (0.7) <sup>6</sup>	0.44	42.8	14	5.2	10.5	60.0	23.3	1.0
4.0%Rh/C (0.2)	0.13	48.8	5.4	0.0	83.6	1.4	0.0	15.0
7.8%Pd/C (0.6)	0.38	60.7	1.9	0.0	99.2	0.2	0.0	0.6
3.0%Ru/C (3.0)	1.88	12.1	0.26	0.0	84.2	6.6	1.2	8.0

<sup>1</sup> 70 °C, 0.20 g catalyst (M/C + SiO<sub>2</sub>), 1.6 kPa DMF partial pressure, 40 mL min<sup>-1</sup> H<sub>2</sub> flow rate. <sup>2</sup> In round brackets, the amount of M/C (mg) in M/C + SiO<sub>2</sub> mixture. <sup>3</sup> DMF conversion and product selectivity at 1 h TOS. <sup>4</sup> TOF values at 1 h TOS. <sup>5</sup> A mixture of *cis* and *trans* isomers (*cis/trans* = 6–10). <sup>6</sup> At 80 °C, 0.10 g catalyst (9.6%Pt/C + SiO<sub>2</sub>).

As seen from Table 2, the total TOF values (s<sup>-1</sup>) decrease in the order 9.6%Pt/C (5.6) > 4.0%Rh/C (5.4) > 7.7%Pd/C (1.9) >> 3.0%Ru/C (0.26) at 70 °C. The TOF value for Pt increased to 14 s<sup>-1</sup> at 80 °C. Our TOF values can now be compared with those reported by Louie et al. [6] for the liquid-phase hydroconversion of DMF in nonane at 80 °C and 5.5 bar H<sub>2</sub> pressure. These TOF values (s<sup>-1</sup>) are as follows: 5%Pt/C (1.77) > 5%Rh/C (0.62) > 10%Pd/C (0.25) >> 5%Ru/C (0.0) (given nominal metal loadings) [6]. 5%Ru/C was not active in liquid phase at 80 °C; it showed a moderate activity at 160 °C (TOF = 0.27 s<sup>-1</sup>) [6]. The two sets of total TOF values are fully comparable. In both cases the rates are unaffected by diffusion limitations. The carbon-supported catalysts are practically the same commercial samples with 3–10% metal loading from Sigma-Aldrich, with metal dispersion measured by CO adsorption using a pulse method and the same stoichiometric coefficients. Given the very close reaction temperature range (70–80 °C), the active sites in both cases are most likely the same if not uniform.

Two facts emerge from these results. First, the TOF values for the gas-phase and liquid-phase reactions follow a similar order: Pt > Rh > Pd >> Ru; albeit the liquid-phase set of TOF shows a greater diversity than the gas-phase set. For the gas-phase reaction, the TOF values for the most active metals, Pt, Rh and Pd, differ by only a factor of three, whereas for the liquid-phase reaction they differ by almost one order of magnitude, apart from Ru, which is far less active. Second and

more important, the TOF values for the gas-phase reaction are about one order of magnitude greater than those for the liquid-phase reaction (note the temperature difference between the gas-phase (70 °C) and liquid-phase (80 °C) results). Hence, the gas-phase process is potentially more efficient than the liquid-phase process. Clarification of the reasons for the higher efficiency of the gas-phase process will require more detailed kinetic studies with systematic variation of reaction parameters. The difference in H<sub>2</sub> concentration in the two systems is not large and should have a relatively small effect on reaction rate. In the liquid-phase system (nonane), [H<sub>2</sub>] = ~0.02 M at 5.5 bar H<sub>2</sub> and 80 °C [6], whereas in our gas phase system, [H<sub>2</sub>] = ~0.04 M in flowing hydrogen at 1 bar H<sub>2</sub> and 70 °C. Given the reaction order in H<sub>2</sub> pressure of ~0.5, this would account for only a factor of 1.4 increase in the rate in the gas phase compared to the liquid phase. The gas-phase system with a low DMF concentration ([DMF] = 5.7 × 10<sup>-4</sup> M) can be viewed as an ideal gas with negligible intermolecular interactions, whereas the condensed liquid-phase system ([DMF] = 1.0 M) [6] is a much more complicated one, involving strong intermolecular forces that may significantly affect the reactivity. In the gas phase, at full DMF conversion, the concentration of reaction products such as 2-hexanone, 2-hexanol and water that could adsorb on the catalysts is less than 10<sup>-3</sup> M, whereas in the liquid phase, even at 10% DMF conversion, it will be 0.1 M, i.e., two orders of magnitude greater. Hence, in the batch liquid-phase system, competitive adsorption of reaction products could both impede the rate and differentiate the activity of metal sites to a greater extent than in the flow gas system.

### 2.3. Hydrogenolysis of Tetrahydrofuran and 2,5-Dimethyltetrahydrofuran

Next, we looked at the gas-phase hydrogenolysis of ring-saturated furan derivatives, THF and DMTHF, over Pt/C and Pd/C catalysts for comparison with the hydroconversion of DMF. These reactions were carried out at 90–100 °C and ambient pressure. Table 3 shows the representative results for THF and Table 4 for DMTHF.

Table 3. Hydrogenolysis of tetrahydrofuran <sup>1</sup>.

Catalyst	W/F (h·g·mol <sup>-1</sup> )	Conversion <sup>2</sup> (%)	Product Selectivity <sup>2</sup> (%)	
			Butane	1-Butanol
9.6%Pt/C + SiO <sub>2</sub> (20)	7.0	0.6	6.5	93.5
7.8%Pd/C + SiO <sub>2</sub> (25)	8.8	0.0		

<sup>1</sup> 100 °C, M/C + SiO<sub>2</sub> catalyst bed (0.20 g total weight, in brackets the amount of M/C in mg), 5.7 kPa THF partial pressure, 20 mL min<sup>-1</sup> H<sub>2</sub> flow, 4 h TOS. <sup>2</sup> Average conversion and product selectivity over 4 h TOS.

Table 4. Hydrogenolysis of DMTHF <sup>1</sup>.

Catalyst	W/F (h·g·mol <sup>-1</sup> )	Temp. (°C)	Conv. <sup>2</sup> (%)	Product Selectivity <sup>2</sup> (%)			
				Hexane	2-Hexanone	2-Hexanol	Other
9.6%Pt/C + SiO <sub>2</sub> (20)	17.3	90	1.6	8.1	1.4	87.6	2.9
9.6%Pt/C + SiO <sub>2</sub> (20)	17.3	100	2.9	7.4	2.7	88.3	1.7
7.8%Pd/C + SiO <sub>2</sub> (25)	21.8	100	0.1	67.0	0.0	0.0	33.0

<sup>1</sup> M/C + SiO<sub>2</sub> catalyst bed (0.20 g total weight, in brackets the amount of M/C in mg), 2.3 kPa DMTHF partial pressure, 20 mL min<sup>-1</sup> H<sub>2</sub> flow, 4 h TOS. <sup>2</sup> Average conversion and product selectivity over 4 h TOS.

As seen from Table 3, THF has negligible reactivity compared to DMF. Pt/C showed a tiny ring-cleavage activity across the C-O bond (0.6% THF conversion), yielding 1-butanol in 94% selectivity at 100 °C. With Pd/C, no reaction was observed at such conditions at all.

DMTHF was more reactive than THF due to the presence of two electron-donating methyl groups (Table 4), yet far less reactive than the aromatic DMF. Again, Pt/C exhibited ring-cleavage activity, yielding 2-hexanol in 88% selectivity at 1.6% and 2.9% DMTHF conversion at 90 and 100 °C, respectively. As expected, Pd/C showed almost no activity (0.1% DMTHF conversion at 100 °C).

The kinetics of the gas-phase hydroconversion of THF and DMTHF over Pt/C was examined at 80 °C and substrate conversion  $\leq 10\%$ . In contrast to DMF, no catalyst deactivation was observed in THF and DMTHF hydroconversion. The reaction rates were determined using average conversion values for 3 h TOS. The hydroconversion of both THF and DMTHF was found to be zero order in the furanic substrate within the range of substrate partial pressure of 0.5–6 kPa. Table 5 shows the TOF values for the hydroconversion of THF, DMTHF and DMF catalysed by Pt/C at 80 °C calculated from zero-order reaction rates. The reactivity of furanic compounds on Pt sites decreases in the order DMF (14)  $\gg$  DMTHF (0.0058) > THF (0.0023), where in round brackets are the TOF values ( $s^{-1}$ ) from Table 5. The aromatic DMF molecule is 2400 times more reactive than its saturated derivative DMTHF. Previously, for gas-phase hydroconversion over Pt/h-BN at 200 °C, Goto et al. [13] reported the reactivity of DMF as only a factor of 30 greater than that of DMTHF. The difference between [13] and our results may be attributed to the difference in reaction temperature. Much greater reactivity of DMF compared to DMTHF suggests an important role of  $\pi$ -bonding between the aromatic DMF molecule and Pt site. As discussed in the Introduction, DFT analysis [15] indicates the key role of  $\sigma$ -bonding between the furan ring and Pt site for the high activity of Pt in the ring cleavage of furanic compounds. From the large difference in reactivity of DMF from DMTHF, initial interaction between DMF and Pt can be suggested to occur via  $\pi$ -bonding followed by rearrangement of  $\pi$ -bonded to  $\sigma$ -bonded DMF, leading to hydrogenolysis of the DMF ring. Much lower reactivity of DMTHF in comparison to DMF gives an additional support to the reaction network shown in Scheme 1, thus confirming the formation of DMTHF and 2-hexanone directly from DMF via independent parallel pathways. On the other hand, the reactivity of DMTHF and THF in hydrogenolysis on Pt sites is quite close, with DMTHF being only two fold more reactive than THF. This points to an enhancement of reactivity by  $\sigma$ -donor methyl groups in DMTHF probably due to strengthening its  $\sigma$ -bonding to the Pt site.

**Table 5.** Total TOF values for Pt-catalyzed hydroconversion of furanic compounds <sup>1</sup>.

Parameter	DMF <sup>2</sup>	DMTHF <sup>3</sup>	THF <sup>4</sup>
W/F ( $g \cdot h \cdot mol^{-1}$ )	0.44	70	42
Conversion (%)	42.8	2.8	0.67
TOF ( $s^{-1}$ ) <sup>5</sup>	14	0.0058	0.0023

<sup>1</sup> 80 °C, 9.6%Pt/C + SiO<sub>2</sub> catalyst bed (0.10 g total weight), 1 h TOS. <sup>2</sup> 9.6%Pt/C (0.7 mg), 1.6 kPa DMF partial pressure, 40 mL min<sup>-1</sup> H<sub>2</sub> flow rate. <sup>3</sup> 9.6%Pt/C (40 mg), 2.3 kPa DMTHF partial pressure, 10 mL min<sup>-1</sup> H<sub>2</sub> flow rate. <sup>4</sup> 9.6%Pt/C (60 mg), 5.7 kPa THF partial pressure, 10 mL min<sup>-1</sup> H<sub>2</sub> flow rate. <sup>5</sup> TOF values at 1 h TOS calculated from zero-order reaction rate  $R = XF/W$  using Pt dispersion  $D = 0.039$  (Table 6).

### 3. Materials and Methods

#### 3.1. Chemicals and Catalysts

2,5-Dimethylfuran (99%) was purchased from Acros Organics (U.S.A.). Tetrahydrofuran (99%) and 2,5-dimethyltetrahydrofuran (*cis/trans* isomer mixture) (96%) were from Sigma-Aldrich (U.K.). Carbon-supported noble metal catalysts with the nominal metal loading of 3–10% were from Sigma-Aldrich (20–80  $\mu m$  particle size). The catalysts were oven dried at 100 °C prior to use. The exact metal loading was determined in-house using inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis after drying: 7.0%Pt/C, 9.6%Pt/C, 7.8%Pd/C, 3.0%Ru/C and 4.0%Rh/C. The catalysts 7.0%Pt/C and 9.6%Pt/C were two samples of the same commercial catalyst with different moisture content. H<sub>2</sub> and CO gases (>99%) were supplied by the British Oxygen Company.

#### 3.2. Techniques

The texture of catalysts (surface area and porosity) was determined from N<sub>2</sub> adsorption measured on a Micromeritics ASAP 2010 instrument at  $-196$  °C. Before measurement, the samples were evacuated for 2–3 h at 250 °C. The ICP-AES analysis was carried out on a Spectro Ciros optical emission spectrometer. Transmission electron microscopy (TEM) analysis of M/C catalysts was performed on a



FEI Tecnai Spirit BioTWIN instrument at 120 kV operation using an Olympus-SIS MegaView III digital camera. The TEM images of M/C catalysts are shown in Figure S4.

Metal dispersion,  $D$ , defined as the fraction of metal at the surface of metal particle,  $D = M_s/M_{\text{total}}$ , was determined via pulse adsorption of CO in He flow at 50 °C on a Micromeritics TPD/TPR 2900 instrument as described elsewhere [20] (10–15 mg catalyst sample, 25  $\mu\text{L}$  pulses of pure CO). The adsorption stoichiometry  $M_s/\text{CO}$  was assumed to be 1 for Pt, Rh, Ru and 2 for Pd [21] as in Louie et al.'s work [6]. Figure S5 shows the measurement of  $D$  for 7.8%Pd/C as an example. Information about the catalysts is presented in Table 6.

**Table 6.** Catalyst characterization.

Catalyst	Surface Area <sup>1</sup> ( $\text{m}^2 \text{g}^{-1}$ )	Pore Volume <sup>2</sup> ( $\text{cm}^3 \text{g}^{-1}$ )	Pore Diameter <sup>3</sup> ( $\text{\AA}$ )	$D$ <sup>4</sup>
7.8%Pd/C	820	0.561	27	$0.326 \pm 0.034$
3.0%Ru/C	1108	0.935	34	$0.232 \pm 0.010$
4.0%Rh/C	830	0.703	34	$0.513 \pm 0.032$
9.6%Pt/C <sup>5</sup>	713	0.558	31	$0.039 \pm 0.007$
7.0%Pt/C <sup>5</sup>	746	0.581	31	$0.039 \pm 0.010$

<sup>1</sup> BET surface area. <sup>2</sup> Single point total pore volume. <sup>3</sup> Average BET pore diameter. <sup>4</sup> Metal dispersion from CO adsorption (average of three measurements). <sup>5</sup> 7.0%Pt/C and 9.6%Pt/C are two samples of the same commercial catalyst with different moisture content.

### 3.3. Catalyst Testing

The hydroconversion of furanic compounds (DMF, THF and DMTHF) was carried out at a gas-solid interface in flowing  $\text{H}_2$  at 70–100 °C and ambient pressure using a Pyrex fixed-bed down-flow reactor (9 mm internal diameter) fitted with an on-line Varian 3800 gas chromatograph with a 30 m  $\times$  0.32 mm  $\times$  0.5  $\mu\text{m}$  Zebron ZB-WAX capillary column and a flame ionisation detector. The catalyst bed was a homogeneous physical mixture of a carbon-supported metal catalyst (M/C) and silica (M/C:SiO<sub>2</sub> = 1:2–1:1000  $w/w$ , 0.20 g total weight). Silica was added to minimise the effect of reaction heat and to keep the size of the catalyst bed constant upon varying the amount of metal catalyst. The gas feed entered the reactor at a flow rate of 20 mL  $\text{min}^{-1}$  unless stated otherwise. The temperature was controlled using a Eurotherm controller ( $\pm 0.5$  °C) with a thermocouple placed on top of the catalyst bed. The furanic substrate was fed by passing  $\text{H}_2$  flow through a saturator, which held the liquid substrate at a certain temperature to keep the chosen reactant at partial pressure. Prior to reaction, the catalysts were pre-treated in situ in  $\text{H}_2$  flow at the reaction temperature for 1 h. The reactions were typically carried out for 4 h time on stream (TOS). Substrate conversion and product selectivity were obtained from on-line GC analysis. The selectivity was determined as moles of product formed per one mole of substrate converted and quoted in % mol. The carbon balance was maintained within 95%. Each catalyst test was repeated at least twice. The mean absolute percentage error in conversion and product selectivity was usually  $\leq 5\%$ . Kinetics of DMF hydroconversion over Pt/C was studied at DMF conversion  $\leq 20\%$ . Reaction rate ( $R$ ) was determined at 1 h TOS as  $R = XF/W$  ( $\text{mol}\cdot\text{g}^{-1}\text{h}^{-1}$ ), where  $X$  is the fractional conversion of DMF,  $W$  is the weight of M/C catalyst (g) and  $F$  is the inlet molar flow rate of furanic substrate ( $\text{mol}\cdot\text{h}^{-1}$ ). Within 1 h TOS, catalyst deactivation was small, with a decline of DMF conversion  $< 10\%$  of the initial  $X$  value. The reaction was found to be zero order in DMF. At such conditions, the rate does not depend on DMF conversion and is equal to the rate constant. Turnover frequency (TOF) was calculated per surface metal site from zero-order kinetics as  $R/M_s$ , where  $M_s$  is the density of surface metal sites in the M/C catalysts ( $\text{mol}\cdot\text{g}^{-1}$ ) calculated from the metal dispersion (Table 6).

## 4. Conclusions

In the past two decades, there has been considerable research activity into the metal-catalysed hydroconversion of furanics ([1–14] and references therein). However, kinetic data is limited, especially

for in the gas-phase hydroconversion. In this work, the gas-phase hydroconversion of 2,5-dimethylfuran (DMF), chosen as a model furanic compound, has been investigated over carbon-supported Pt, Pd, Rh and Ru catalysts in a fixed-bed reactor at 70–90 °C and ambient pressure. The total turnover frequency (TOF) of metal sites in the gas-phase DMF hydroconversion, including ring-opening and ring-saturation pathways, has been determined from zero-order kinetics in the absence of diffusion limitations. The TOF values decrease in the sequence Pt > Rh > Pd >> Ru. Previously, Louie et al. [6] reported the total TOF values for the same catalysts in liquid-phase hydroconversion of DMF in a batch reactor. Comparison of the two sets of TOF leads to the following conclusions. First, the TOF values for the gas-phase and liquid-phase reactions follow the same order, albeit the liquid-phase TOFs show a greater diversity. Second and more important, the TOF values for the gas-phase reaction are about one order of magnitude greater than those for the liquid-phase reaction. The gas-phase process, therefore, is potentially more efficient than the liquid-phase process. Ring-saturated furan derivatives, THF and DMTHF, are much less reactive than the aromatic DMF in the gas-phase hydroconversion on Pt/C, with the TOF values decreasing in the order DMF >> DMTHF > THF. Much greater reactivity of DMF compared to DMTHF suggests the importance of  $\pi$ -bonding between DMF and the Pt site and gives an additional support to the formation of DMTHF and 2-hexanone directly from DMF via independent parallel pathways.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/10/10/1171/s1>, Figure S1: Long-term stability test, Figure S2: Catalyst deactivation plot, Figure S3: Catalyst regeneration, Figure S4: TEM images of metal catalysts, Figure S5: Measurement of metal dispersion by adsorption of CO, Weisz-Prater analysis.

**Author Contributions:** I.V.K. and E.F.K. conceived, designed and supervised the experiments; H.A. and C.K.-O. performed the experiments; H.A. analyzed results and drafted the paper; I.V.K. edited the paper. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Acknowledgments:** We thank the Deanship of Scientific Research at King Faisal University, Saudi Arabia for the financial support under Nasher Track (Grant No. 186372).

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502. [[CrossRef](#)] [[PubMed](#)]
2. Román-Leshkov, Y.; Chheda, J.N.; Dumesic, J.A. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* **2006**, *306*, 1933–1937. [[CrossRef](#)] [[PubMed](#)]
3. West, R.M.; Liu, Z.Y.; Peter, M.; Dumesic, J.A. Liquid alkanes with targeted molecular weights from biomass-derived carbohydrates. *ChemSusChem* **2008**, *1*, 417–424. [[CrossRef](#)] [[PubMed](#)]
4. Huber, G.W.; Chheda, J.N.; Barrett, C.J.; Dumesic, J.A. Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* **2005**, *308*, 1446–1450. [[CrossRef](#)] [[PubMed](#)]
5. Brentzel, Z.J.; Barnett, K.J.; Huang, K.; Maravelias, C.T.; Dumesic, J.A.; Huber, G.W. Chemicals from biomass: Combining ring-opening tautomerization and hydrogenation reactions to produce 1,5-pentanediol from furfural. *ChemSusChem* **2017**, *10*, 1351–1355. [[CrossRef](#)] [[PubMed](#)]
6. Louie, Y.L.; Tang, J.; Hell, A.M.L.; Bell, A.T. Kinetics of hydrogenation and hydrogenolysis of 2,5-dimethylfuran over noble metals catalysts under mild conditions. *Appl. Catal. B* **2017**, *202*, 557–568. [[CrossRef](#)]
7. Kliewer, J.; Aliaga, C.; Bieri, M.; Huang, W.; Tsung, C.-K.; Wood, J.B.; Komvopoulos, K.; Somorjai, G.A. Furan hydrogenation over Pt(111) and Pt(100) single-crystal surfaces and Pt nanoparticles from 1 to 7 nm: A kinetic and sum frequency generation vibrational spectroscopy study. *J. Am. Chem. Soc.* **2010**, *132*, 13088–13095. [[CrossRef](#)] [[PubMed](#)]
8. Kang, J.; Vonderheide, A.; Guliants, V.V. Deuterium-labeling study of the hydrogenation of 2-methylfuran and 2,5-dimethylfuran over carbon-supported noble metal catalysts. *ChemSusChem* **2015**, *8*, 3044–3047. [[CrossRef](#)] [[PubMed](#)]

9. Runnebaum, R.C.; Nimmanwudipong, T.; Doan, J.; Block, D.E.; Gates, B.C. Catalytic conversion of furan to gasoline-range aliphatic hydrocarbons via ring opening and decarbonylation reactions catalyzed by Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. *Catal. Lett.* **2012**, *142*, 664–666. [[CrossRef](#)]
10. Kang, J.; Liang, X.; Gulians, V.V. Selective hydrogenation of 2-methylfuran and 2,5-dimethylfuran over atomic layer deposited platinum catalysts on multiwalled carbon nanotube and alumina supports. *ChemCatChem* **2017**, *9*, 282–286. [[CrossRef](#)]
11. Corma, A.; de la Torre, O.; Renz, M.; Villandier, N. Production of high-quality diesel from biomass waste products. *Angew. Chem. Int. Ed.* **2011**, *50*, 2375–2378. [[CrossRef](#)] [[PubMed](#)]
12. Yang, J.; Li, S.; Zhang, L.; Liu, X.; Wang, J.; Pan, X.; Li, N.; Wang, A.; Cong, Y.; Wang, X.; et al. Hydrodeoxygenation of furans over Pd-FeO<sub>x</sub>/SiO<sub>2</sub> catalyst under atmospheric pressure. *Appl. Catal. B* **2017**, *201*, 266–277. [[CrossRef](#)]
13. Goto, H.; Takagaki, A.; Kikuchi, R.; Oyama, S.T. Hydrogenation of 2,5-dimethylfuran on hexagonal-boron nitride- and silica-supported platinum catalysts. *Appl. Catal. A* **2017**, *548*, 122–127. [[CrossRef](#)]
14. Tong, T.; Xia, Q.; Liu, X.; Wang, Y. Direct hydrogenolysis of biomass-derived furans over Pt/CeO<sub>2</sub> catalyst with high activity and stability. *Catal. Commun.* **2017**, *101*, 129–133. [[CrossRef](#)]
15. Vorotnikov, V.; Vlachos, D.G. Group additivity and modified linear scaling relations for estimating surface thermochemistry on transition metal surfaces: Application to furanics. *J. Phys. Chem. C* **2015**, *119*, 10417–10426. [[CrossRef](#)]
16. Boudart, M. Turnover rates in heterogeneous catalysis. *Chem. Rev.* **1995**, *95*, 661–666. [[CrossRef](#)]
17. Mihailovic, M.L.; Mamuzic, R.I.; Zigic-Mamuzic, L.; Bosnjak, J.; Cekovic, Z. Assignment of cis-trans configuration to constitutionally symmetrical 2,5-dialkyl-tetrahydrofurans. *Tetrahedron* **1967**, *23*, 215–226. [[CrossRef](#)]
18. Bond, G.C. *Metal-Catalysed Reactions of Hydrocarbons*; Springer: New York, NY, USA, 2005.
19. Weisz, P.B.; Prater, C.D. Interpretation of measurements in experimental catalysis. *Adv. Catal.* **1954**, *6*, 143–196.
20. Alharbi, K.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Hydrogenation of ketones over bifunctional Pt-heteropoly acid catalyst in the gas phase. *Appl. Catal. A* **2015**, *504*, 457–462. [[CrossRef](#)]
21. Canton, P.; Fagherazzi, G.; Battagliarin, M.; Menegazzo, F.; Pinna, F.; Pernicone, N. Pd/CO average chemisorption stoichiometry in highly dispersed supported Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. *Langmuir* **2002**, *18*, 6530–6535. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).