Abstract Hexavalent chromium is widely used in industry and causes human health and environmental problems due to its extremely toxic properties. On the contrary, trivalent chromium is necessary for living ecosystems. Therefore, reducing hexavalent chromium to trivalent chromium is the best strategy for detoxifying hexavalent chromium. Pd(0)@C nanocatalyst was prepared by a simple impregnation-reduction method in solution under mild conditions at 298 K and was identified by XPS, XRD, TEM, TEM–EDX, HR-TEM, and ICP-OES analyses. TEM results showed that very well-dispersed Pd nanoparticles were formed on the C surface (mean particle sizes 3.98 ± 0.24 nm). The catalytic performance of Pd(O)NPs impregnated on cheap and easily available commercial activated carbon were tested as heterogeneous nanocatalysts in the catalytic reduction of hexavalent chromium in the medium of formic acid, which is a good reducing agent, and sodium formate as the promoter at 298 K. It was determined that the formed Pd(0) nanoclusters could successfully reduce Cr(VI) to Cr(III) with high selectivity (~97%) in formic acid and sodium formate solution under mild conditions. It was also observed that the Pd(0)@C catalyst retained a significant (>75%) initial activity even after the 5th use. In addition, the kinetic studies of the catalytic reduction reaction of Cr(VI) catalyzed by Pd(0)@C nanoparticles were investigated depending on the substrate [Cr₂O₇²⁻], catalyst [Pd(0)@C], sodium formate [HCOONa], formic acid [HCOOH] concentrations, and temperature parameter. From the rich kinetic data obtained, the nature of the velocity equation was explained, and the activation parameters were calculated.

Keywords Chromium · Formic acid · Nanocatalyst · Palladium · Reduction · Kinetic

1 Introduction

The element chromium, which ranks 22nd in terms of abundance in the earth’s crust, is used in various industrial and commercial applications (such as textile manufacturing, wood protection, metallurgy, metal plating, pigment production, corrosion inhibition, and electroplating). Industrial wastewater containing chromium compounds is discharged into the natural environment without treatment and inappropriately (Doan et al., 2015; Hashim et al., 2011; Chen et al., 2016; Parabhakaran et al., 2009; Chen et al., 2013; Keith & Telliard, 1979; Kotas & Stosicka, 2000). Cr(VI)-containing industrial wastewater is considered as the second heavy metal...
pollutant (Yadav & Xu, 2013). Cr(VI) has proven to be a mutagenic, acute toxicity carcinogen in its compounds (Elliott & Zhang, 2001; Gheju, 2011; Stearns et al., 1995; Zhang & Yang, 2019). Chromium(VI) has been recognized as a priority pollutant by the US Environmental Protection Agency and many countries (Fernández et al., 2010). In the World Health Organization guideline, it is emphasized that the level of hexavalent chromium in drinking water should be less than 0.05 mgL$^{-1}$ (WHO, 2008). Trivalent chromium on the other hand, less mobile in nature, is less toxic and is necessary nutrition for living things in lesser amounts (Celebi et al., 2016; Xu et al., 2015; Zhиткович, 2011; Kyung et al., 2005). Various treatment methods such as electrochemical oxidation, membrane separation, ion exchange, chemical extraction, adsorption, precipitation, and reduction have been developed to remove Cr(VI) from the wastewater environment (Bertoni et al., 2014; Chauhan et al., 2012; Jiang et al., 2017; Rajiv Gandhi & Meenakshi, 2013; Yu et al., 2020). Among these, reduction of Cr(VI) is preferred as a common and applicable method (Jiang et al., 2017; Okello et al., 2012). Therefore, it is a good idea to detoxify hexavalent chromium by reducing it to trivalent chromium (Celebi et al., 2016).

Recently, scientists in the related fields have focused on the development and applications of new, environmentally friendly catalytic materials for the reduction of Cr(VI) to C(III) (Veerakumar et al., 2017). They tested various catalytic materials such as different organic structures, Fe(II)-based minerals, bacterial strains, ZnO nanorods and sulfides in the reduction of Cr(VI) (Celebi et al., 2016; Lan et al., 2005; Shirzad-Sibani et al., 2014; Hsu et al., 2010; Buerge et al., 1998). Transition metal NPs have been in great demand recently due to their superior performance in the catalyzed reduction reaction of Cr(VI) (Barakat et al., 2013; Celebi et al., 2016; Zähmakiran & Ozkar, 2011). In particular, nanoparticle catalysts such as amino-functionalized palladium nanowires (Wei et al., 2015), PSA-supported palladium nanoparticles (Fu et al., 2014), polyacrylic acid (PAA)-stabilized Pd nanoparticles (Omole et al., 2007), Pd NPs supported on amine-functionalized SiO$_2$ (Celebi et al., 2016), and poly(vinylpyrrolidone) (PVP)-immobilized palladium nano-tetrapods showed high activity in reducing hexavalent chromium in the presence of reducing agent HCOOH (FA) (Omole et al., 2007). When formic acid is combined with metal NPs, high efficiency of Cr(VI) catalytic reduction is obtained. Much different from other monocarboxylic acids, using Pd NPs completely mineralizes formic acid to CO$_2$ and H$_2$ (HCOOH→CO$_2$+H$_2$), and the released H$_2$ reduces Cr(VI) at faster rates (Celebi et al., 2016; Dandapat et al., 2011; Omole et al., 2007; Yadav & Xu, 2012; Yurderi et al., 2014). Then, the released H$_2$ is stabilized on the palladium nanoparticles, and Cr(VI) is reduced to Cr(III) (Cr$_2$O$_7^{2-}$+8H$^+$+3H$_2$→2Cr$^{3+}$+7H$_2$O) (Celebi et al., 2016; Fu et al., 2014; Huang et al., 2012). However, aggregation occurs in the active centers of colloidal Pd nanoparticles due to their multiple use, which reduces their activity (Fu et al., 2014; Omole et al., 2007; Wei et al., 2015). In order to prevent agglomeration on the surfaces of Pd NPs and to easily separate them from the solution, the idea of impregnating Pd NPs on or into the surface of the support was accepted (Celebi et al., 2016; Dandapat et al., 2011; Elliott & Zhang, 2001; Huang et al., 2012; Liang et al., 2013; Yang et al., 2010). Therefore, many different solid support materials are now preferred to stabilize guest palladium nanoparticles. Yadav et al. (Yadav & Xu, 2013) stabilized Pd nanoparticles on MIL-101 metal–organic framework to isolate Cr(VI) from industrial wastewater. Huang and coworkers (Huang et al., 2012) used Pd NPs as a reusable catalyzed material for the reduction reaction of Cr(VI) under mild conditions by impregnation on electrospun polymer nanofibers. Dandapat and coworkers (Dandapat et al., 2011) used mesoporous γ-Al$_2$O$_3$ films prepared after hydrolysis of peptization of Al(OOH) as support material for Pd NPs. Nanoparticles stabilized on suitable support materials prevent metal aggregation, reduce metal loading, increase electrochemical stability and activity, and prolong catalyst life (Wei et al., 2015; Yurderi et al., 2014). Therefore, it is important to develop new Pd NPs catalysts supported in suitable support material to increase the reduction rate of hexavalent chromium (Celebi et al., 2016). In particular, high surface area multi-walled carbon nanotubes (MWCNTs) consisting of several concentric graphene tubes with a diameter of 100 nm (Köktürk et al., 2019), carbon nanofibers, carbon derivatives containing carbon nanofibers, carbon black, graphite, carbon nanotubes, graphene, and its derivatives are excellent support materials due to their excellent strength, superior stability, and large
surface areas (Demir et al., 2017). Activated carbon, cellulose, and silica gel are also widely used as support materials (Demirbaş et al., 2019). Therefore, we developed the previously unused Pd@C catalyst for the reduction reaction of Cr(VI) in the FA medium.

2 Materials and Methods

2.1 Devices and Materials

Sodium formate (HCOONa), formic acid (HCOOH), NiCl₂·6H₂O, RuCl₃·3H₂O, Pd(NO₃)₂·2H₂O (∼40% Pd), activated carbon (C), sodium borohydride (NaBH₄), sodium hydroxide (NaOH), potassium dichromate (K₂Cr₂O₇), and ethanol (C₂H₅OH) were purchased from Sigma-Aldrich®. Nuve FN 300 oven (0–2500 °C), Heidolph MR-3004 magnetic stirrer, Lab Companion RW-0525 temperature bath, and Shimadzu UV-2600 DR/UV–vis.

2.2 Preparation of the Catalysts (Pd@C, Ni@C, Ru@C)

Nanocatalysts were synthesized in a simple and reproducible manner by conventional impregnation and simultaneous reduction method of Pd, Ru, and Ni metals on activated carbon (C) (Celebi et al., 2016; Yang et al., 2010; Zhu & Xu, 2015).

(a) Pd@C synthesis; Pd metal was supported on 100 mg C in 5.0 mg water (Pd(NO₃)₂·2H₂O (4.95 mg, 19.20 µmol Pd) (mixed at 700 rpm for 2 h)) and reduced with NaBH₄ (11.12 mg, 0.3 mM).

(b) Ru@C synthesis; Ru metal was supported on 100 mg C in 5.0 mg water (RuCl₃·3H₂O (5.28 mg, 20.18 µmol Ru) (mixed at 700 rpm for 2 h)) and reduced with NaBH₄ (11.69 mg, 0.32 mM).

(c) Ni@C synthesis; Ni metal was supported on 100 mg C in 5.0 mg water (NiCl₂·6H₂O (8.32 mg, 35 µmol Ni) (mixed at 700 rpm for 2 h)) and reduced with NaBH₄ (20.16 mg, 0.54 mM).

Then the mixtures were filtered and washed with plenty of water (3×10 mL); nanocatalysts were obtained in powder form and dried in a vacuum oven at 150 °C for 1 h.

2.3 Catalytic Experiments

K₂Cr₂O₇ solution (10 mL, 2.0 mM, 5.89 mg) was transferred to the reaction vessel, 10.0 mg of Pd(0)@C nanocatalyst was added, and the reaction was equilibrated at 298 K for 15 min. Then, 1.0 mL solution (HCOONa; 312.3 mg, 450 M + HCOOH; 173.2 µL 0.45 M) was transferred to the reaction vessel with a 1.0-mL gas-insulated syringe. Immediately after, the catalyzed reaction was initiated with turning on the stirrer (>700 rpm), at 0 min, and then at certain time intervals, 0.9 mL of solution was taken from the sample cup, diluted to 1.0 mL with water, and read in UV (Shimadzu UV-2600 spectrometer).

2.4 Identification of Gaseous Products from the Decomposition of Formic Acid Over Pd@C Catalyst

Before beginning the catalytic reaction of FA, the hot water bath (Lab Companion RW-0525) was adjusted to a constant temperature of 25 °C, and a Schlenk type jacketed reaction vessel (50.0 mL) was fixed onto a magnetic stirrer (Heidolph MR-3004). Ten milligrams of Pd(0)@C nanocatalyst was transferred to a Schlenk type reaction vessel, 9.0 mL of H₂O was added, and it was allowed to reach thermal equilibrium at 298 K for 15 min. Next, 1.0 mL of formic acid + sodium formate solution (450 mM FA + 450 mM SF) was transferred to the reaction vessel, and the catalyzed reaction was initiated by operating the stirrer (>700 rpm) (t = 0 min). The resulting gas was collected in the GC flask and analyzed with the Shimadzu TCD-2014 GC.

2.5 NaOH Trap Test

The trap test was carried out to determine the selectivity of the catalyst used in the catalytic decomposition reaction of FA. The trap experiment will give information about whether the reaction is proceeding through dehydrogenation or dehydration. Some researchers (Celebi et al., 2016; Gu et al., 2011; Yadav et al., 2012) have performed the NaOH trap experiment. The gas released from the dehydrogenation of FA is passed through a saturated NaOH (10.0 M) solution before the gas burette. When the reaction takes place with high selectivity since all of the CO₂ gas formed together with the H₂ gas will

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react with NaOH in the trap, the gas volume to be measured should be halved (2NaOH(aq) + CO₂(g) → Na₂CO₃(aq) + H₂O(s)).

2.6 UV–vis Spectroscopic Studies

The absorption peak of hexavalent chromium was measured with UV–vis spectroscopy at a fixed wavelength at 350 nm. Calculation of the concentration of remaining hexavalent chromium was made with a calibration curve obtained from the absorbance of standard solutions. The degree of catalytic reduction, also referred to as a cycle, was calculated from the equation Conversion = [Cr(VI)]/([Cr(VI])₀. Here, [Cr(IV)]₀ and [Cr(VI)] are the initial and specific times, respectively.

2.7 Confirmation of the Presence of Cr(III) as a Catalytic Reaction Product

Extra NaOH was transferred to the solution resulting from the conversion of hexavalent chromium, forming a green-colored hexahydroxochromate(III) solution, confirming the formation of Cr(III) in solution (Bulut et al., 2015; Celebi et al., 2016; Yang et al., 2010; Zhu & Xu, 2015).

2.8 Reusability Performance

After the first catalytic cycle, the catalyst (Pd@C) was purged from the solution medium, dried, and used in the next cycle. The number of cycles was repeated up to 5.

2.9 Kinetic Studies

2.9.1 Effects of Sodium Formate [HCOONa], Formic Acid [HCOOH], Dichromate [Cr₂O₇²⁻], Catalyst [Pd(0)@C] Concentrations and Temperature on the Catalytic Reduction of Cr(VI) to Cr(III)

The effects of FA (0, 122.5, 225, 450, 675 mM), SF (0, 122.5, 225, 450, 675 mM), dichromate (1.0, 2.0, 4.0, 8.0 mM), and catalyst (5.0, 7.5, 10.0, 15.0 mg Pd(0)@C, 1.37% by weight Pd loadings correspond to 0.065, 0.098, 0.129, 0.196 mM Pd) initial concentrations and temperature (298–318 K) onto the catalytic reduction of Cr(VI) to trivalent chromium were investigated.

2.9.2 The Superiority of Pd(0)@C Catalyst

To determine the superiority of Pd(0)@C catalyst over Ru(0)@C and Ni(0)@C nanocatalysts, the reduction of Cr(VI) was investigated in the same test standards (10.0 mL water; 312.3 mg, 450 mM HCOONa; 173.2 µL, 450 mM HCOOH; 2.0 mM, 5.89 mg K₂Cr₂O₇) and 298 K.

3 Results and Discussion

3.1 Characterization of Pd NPs Stabilized on Activated Carbon (C)

The nature of the prepared Pd@C nanoclusters was described using P-XRD, ICP-OES, DR/UV–vis, TEM–EDX, HRTEM, and XPS techniques. The Pd ratio in the Pd(0)@C catalyst was determined by ICP-OES (1.37 wt% Pd) (Celebi et al., 2016; Liang et al., 2013; Yang et al., 2010; Zhu & Xu, 2015). Figure 1 presents the P-XRD patterns of C and Pd@C. When the Pd(0)@C and C peaks are examined carefully, it is seen that there is a decrease from the Pd(0)@C peaks compared to the C peaks (Fig. 1). The decrease in the specific BET surface was determined as 200 m²/g for C and 150 m²/g for Pd(0)@C. This decrease in the BET surface of

![Fig. 1](a) C and (b) Pd(0)@C patterns of P-XRD in the 2Θ = 10–80° range
Pd(0)@C indicates that Pd NPs are supported on C. It is seen that it gives diffraction peaks at 39.6°, 46.5°, and 67.8° on the 111, 200, and 220 surfaces of Pd, respectively (JCPDS No. 05–0681) (JCPDS, 1991) (Fig. 1). XPS analyses were performed to define the oxidation steps of the Pd metal in the sample (Fig. 2). Signals were observed for Pd$^{0}$3$d_{5/2}$ and Pd$^{0}$3$d_{3/2}$ at binding energies of 334.5 and 339.8 eV, respectively (Fig. 2) (Yang et al., 2010; Celebi et al., 2016; Zhu & Xu, 2015; Zhang et al., 2013; Abass et al., 2005). TEM, TEM–EDX, and HRTEM analysis techniques were used to describe the average particle size, crystal structure, and morphology of the activated carbon stabilized Pd(0)@C catalytic material. The presence of well-dispersed palladium NPs onto the C surface was revealed by TEM (Fig. 3a). The histogram shows the palladium NPs size ranging from 2.06 to 5.3 nm and the average palladium NPs size of 3.98 nm (Fig. 3b). The TEM–EDX spectrum shows the existence of Pd, O, and C atoms in the sample (Fig. 3c). The HRTEM image shows that the Pd nanoclusters formed in high crystallinity (Fig. 3d). The Pd fringe spacing was determined as 0.223 nm and 0.139 on the Pd(111) and Pd(200) surfaces, respectively (Celebi et al., 2016; Schlotterbeck et al., 2014; Su et al., 2015; Yang et al., 2014; Zhang et al., 2013; Zhu & Xu, 2015).

### 3.2 Control Experiments for the Pd(0)@C Catalyzed Decomposition Reaction of Formic Acid

As in many studies, sodium formate was used as a trigger for the catalytic degradation reaction of FA (Celebi et al., 2016; Gu et al., 2011; Wei et al., 2015; Yadav & Xu, 2012; Yurderi et al., 2014). Recent reports suggest that some homogeneous (Kim et al., 2014; Su et al., 2015) and heterogeneous (Celebi et al., 2016; Yang et al., 2010) catalysts may obtain H$_2$ not only from formic acid but also from catalyzed hydrolysis of sodium formate (HCOONa + H$_2$O $\rightarrow$ H$_2$ + NaHCO$_3$). To determine whether the resulting gas is from FA or SF, it must be confirmed by a control test. In the control experiment, we found that hydrolysis of SF released only 2.2 mL of H$_2$ gas even at 230 min at 318 K. It is significant to determine whether the Cr(VI) catalytic reduction reaction proceeds in the dehydrogenation (HCOOH $\rightarrow$ CO$_2$ + H$_2$) pathway of FA or in the dehydration (HCOOH $\rightarrow$ H$_2$O + CO) pathway (Celebi et al., 2016; Enthaler et al., 2010; Zahmakiran et al., 2012). Because in trivalent chromium catalytic reduction, both H$_2$ (Celebi et al., 2016; Roucoux et al., 2002) and CO (Cannors, 1990) can act as reducing agents. Therefore, NaOH trap test and GC/TCD analysis were carried out to define the selectivity of Pd(0)@C nanocatalyst in the degradation reaction of FA (Celebi et al., 2016; Gu et al., 2011; Liang et al., 2013; Yadav & Xu, 2012; Yurderi et al., 2014). At the end of the NaOH trap, it was seen that the total volume of gas produced was halved (Fig. S1).

### 3.3 Monitoring of Catalytic Reduction Reaction and Reactivity of Catalytic Palladium-Free C

The effect onto the catalytic performance of nanocatalyst (Pd(0)@C) onto the reaction rate in the reduction of Cr(VI) was determined with many experiments. K$_2$Cr$_2$O$_7$ was preferred as the hexavalent chromium source. The characteristic peak of Cr(VI) due to the charge transfer transition (LMCT) from ligand (oxygen) to metal (Cr(VI)) was measured at 350 nm at a fixed wavelength (Celebi et al., 2016; Gu et al., 2011; Liang et al., 2013; Wei et al., 2015; Yadav & Xu, 2012; Yang et al., 2010; Yurderi et al., 2014). This makes it possible to study the reduction processes of Cr(VI) with UV–vis. Before starting testing the activity of the Pd(0)@C catalytic

![Fig. 2 XPS of Pd(0)@C the survey spectrum](image-url)
material, the catalytic activity of the activated carbon support material was tested. It was observed that the characteristic peak at 350 nm remained constant for 70 min without loading Pd NPs. It was observed that the absorption peak at 350 nm remained unchanged for 70 min without Pd NPs (Fig. 4a). This indicates that reduction cannot occur without Pd NPs. When a very small amount of Pd NPs (10.0 mg Pd(0)@C, 1.29 µmol Pd) was loaded onto the C solid support, the characteristic absorption peak at 350 nm was completely reduced at 65 min (Fig. 4b). Initially yellow, the potassium dichromate solution turned into a colorless solution after completing the catalytic cycle. The presence of Cr(III) was confirmed with transferring NaOH to this colorless solution. It was observed that the color of the colorless solution turned green with NaOH transfer. This shows the formation of hexahydroxochromic(III) ([Cr(OH)6]−3), which is evidence of the presence of Cr(III). The pH of the catalytic reduction was also observed. It was found that
the pH of the solution was 3.58 at the beginning, then increased to 3.62, and remained stable at this value until the catalytic cycle was completed.

3.4 Uniqueness of Pd(0)@C in the Catalytic Reduction of Cr(VI) to Cr(III)

In this study, easily available and inexpensive C was preferred as solid support material. In the catalytic reaction, the superiority of Pd metal was investigated by comparing it with Ru and Ni metals. The catalytic activities of Pd(0)@C, Ru(0)@C, and Ni(0)@C nanocatalysts in Cr(VI) reduction were tested. With Ru (10.0 mg; 1.37% Ru, 1.36 µmol Ru) and Ni (10.0 mg; 1.40% Ni, 2.38 µmol Ni) metal loading, the characteristic peak of Cr(VI) at 350 nm remained constant up to 70 min (Figs. S2 and S3); on the contrary, Pd metal loading (10.0 mg; 1.37% Pd, 1.29 µmol Pd) was completely reduced in 65 min (Fig. S4). This indicates that the activity of palladium nanoparticles is higher for this reaction.

3.5 Catalytic Stability of Pd@C in the Catalytic Reduction of Cr(VI)

The stability of the Pd(0)@C nanocatalyst was tested in the reduction of Cr(VI) for purification from solution and reusability. After the 1st catalytic cycle is complete (Fig. 5a), the catalyst was removed from the solution medium and used in the next conversion. The number of catalytic conversions was repeated as 5, and it was found that it retained >75% of its initial activity even after the 5th catalytic conversion (Fig. 5b). The TEM image of the 5th catalytic cycle is given in Fig. 5c, and the average particle size obtained from this TEM image was determined as 5.30 nm (Fig. 5d). The average Pd NPs size appears to have increased from 3.98 ± 0.24 (fresh) to 5.30 ± 0.21 nm (at the end of the 5th conversion), hence a slight increase in particle size. This increase indicates a decrease in the activity of the nanocatalyst. In addition, Pd metal was not found in the 5th catalytic cycle ICP-OES analysis, indicating that Pd nanoclusters were supported on the C support material without leaking into the solution.

3.6 Kinetic Studies

For the catalytic reduction of Cr(VI), kinetic studies were first initiated by attempts to determine the most effective ratios of [FA] (Fig. S5) and [SF] (Fig. S6) concentrations. Figure 6a and c shows the remaining of Cr(VI) fraction to initial concentration ([Cr(VI)]/ [Cr(VI)]₀) against time. It was determined that Cr(VI) was not reduced to Cr(III) when FA was not added to the catalytic reaction but gradually reduced when SF was not added, and adding FA up to 0.45 M increased the reaction rate, but did not increase the reaction rate at further concentrations (as in reaction kinetics) (Celebi et al., 2016; Zahmakiran & Ozkar, 2006) (Fig. 6b). It was observed that increasing the
concentration of SF up to 0.45 M played a triggering (p) role onto the reduction rate of Cr(VI) to Cr(III), but adding more than 0.45 M decreased the reduction rate (Fig. 6d). The reason for this may be explained with the formate anion poisoning the surfaces of the active Pd centers (Durap et al., 2009; Zahmakiran & Ozkar, 2006). Therefore, in this study, FA/SF concentrations were kept constant at 0.45 M/0.45 M, which is the most effective ratio. The graph of the Cr(VI) fraction remaining in solution ([Cr(VI)/[Cr(VI)]₀]) against time, created with diverse Pd concentrations (Fig. S7), is given in Fig. 7a. The observed rate constants (kₐₒ_sb) of catalytic reduction of Cr(VI) were obtained from the linear sections of the graph in Fig. 7a. The graph of the In kₐₒ sb against ln[Pd] is given in Fig. 7b. According to the 1.39 slope of Fig. 7b, the catalytic reduction takes place in the first order depending on the concentration of Pd. The ratio of Cr(VI) remaining in solution ([Cr(VI)/[Cr(VI)]₀]) against time, generated from diverse initial concentrations of Cr₂O₇ (Fig. S8), is given in Fig. 7c. In kₐₒ sb against the In[Cr₂O₇²⁻] substrate concentration is given in Fig. 7d. Considering the slope of this graph, it is seen that the catalytic reduction takes place by a slope of 0.23° depending on the dichromate concentration.

In addition, the effect of temperature as well as substrate and palladium nanoparticles concentrations onto the reduction rate of the catalyzed reaction was investigated. The effect of temperature onto the reduction rate of Cr(VI) has been investigated in many experiments at different temperatures
(298–318 K) (Fig. S9). UV–vis spectroscopy of Cr(VI) catalytic conversion at 298, 303, 308, 313, and 318 K at \( t = 1 \) min is given in Fig. 8a. It seems that the reduction ratio of Cr(VI) increases as the temperature increases. Figure 8b indicates the graph of the fraction of Cr(VI) remaining in solution (\( [\text{Cr(VI)}]/[\text{Cr(VI)}]_0 \)) against time, obtained at different temperature range (298–318 K). The activity values of Pd(0)@C catalyst at 298, 303, 308, 313, and 318 K temperatures were determined as 31, 33, 36, 47, and 57 mol Cr_2O_7^{2−}/mol Pd min, respectively. These activity values are higher than the activity values of PdNPs@polymer nanofibers (at 323 K, 2.32 mol Cr_2O_7^{2−}/mol Pd min) (Huang et al., 2012), palladium tetrapods (at 323 K, 4.23 mol Cr_2O_7^{2−}/mol Pd min) (Celebi et al., 2016; Fu et al., 2014), and supported Pd/PtNPs (at 318 K, 1.66 mol Cr_2O_7^{2−}/mol Pd min) (Liang et al., 2014). Arrhenius graph (Fig. 8c) and Eyring-Polanyi graph (Fig. 8d) were drawn from the \( k_{\text{obs}} \) calculated from the graphs of five different temperatures (Fig. 8b). Then, the activation parameters \( E_a \) from the Arrhenius graph, \( \Delta H^a \), and \( \Delta S^a \) from the Eyring-Polanyi graph were calculated. For the Pd(0)@C catalyst, the activation values of \( E_a \), \( \Delta H^a \), and \( \Delta S^a \), respectively, were calculated as 39.0 kJ/mol, 53.4 kJ/mol, and \(-210.0\) J/mol K. The activation enthalpy (39.0 kJ/mol) obtained from the reduction of Cr(VI) with Pd(0)@C is lower than that obtained in the existence of Pd@γ–A12 O3 catalyst (76.2 kJ/mol) (Celebi et al., 2016; Dandapat et al., 2011; Huang et al., 2012; Yang et al., 2010). The low positive activation enthalpy and negative activation entropy show that the reduction of Cr(VI) with Pd(0)@C catalyst occurs by a transitional associative mechanism.

4 Conclusions

In summary, Pd^{2+} particles were supported on activated carbon in solution, followed by reduction to
Pd(0) with NaBH4 under mild conditions, to synthesize the Pd(0)@C nanocatalyst in a simple and reproducible manner. Then characterization was performed by P-XRD, ICP-OES, HRTEM, DR/UV–vis, TEM–EDX, and XPS. The results of the analysis showed that very well-dispersed palladium nanoparticles (average particle size 3.98 nm) were formed on the activated carbon. The durability, catalytic performance, and activity of the Pd(0)@C nanocatalyst were investigated in the catalytic reduction of Cr(VI) to Cr(III) in FA medium as a reducing agent at 298 K. The Pd(0)@C catalyst showed to be a heterogeneous nanocatalyst with usable activity (TOF = 31 mol Cr₂O₇²⁻/mol Pd min) in the catalytic reaction. Moreover, the first synthesized Pd(0)@C nanocatalyst proved to have outstanding resistance to solution seepage and aggregation, retaining > 75% of its initial activity even after the 5th catalytic cycle. As a result, we believe that the Pd(0)@C catalyst will lead to the synthesis of new catalysts.

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Data Availability All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Conflict of Interest The authors declare no competing interests.
Fig. 8  a UV–vis spectroscopy of Pd(0)@C catalyst at \( t = 1 \) min, b graph of remaining Cr(VI) ratio ([Cr(VI)]/[Cr(VI)]\text{0}) against time, c plots of Arrhenius, and d Eyring-Polanyi obtained from the data in b

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