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Catalytic Low-Temperature Combustion of Dichloromethane over V-Ni/TiO$_2$ Catalyst:

A plausible pathway for DCM oxidation over V-Ni/TiO$_2$, Xinhua Zhang, Zhiying Pei, Xinjie Ning.

Hanfeng Lu, Haifeng Huang, RSC Advances
Catalytic Low-Temperature Combustion of Dichloromethane over V-Ni/TiO₂ Catalyst

Xinhua Zhang¹, Zhiying Pei¹, Xinjie Ning², Hanfeng Lu¹, Haifeng Huang¹,*

Vanadium–nickel mixed oxides supported on TiO₂ (anatase) were prepared by wet impregnation using ammonium metavanadate and nickel nitrate aqueous solution. The performance of as-prepared samples in catalytic dichloromethane (DCM) combustion was investigated, and their physicochemical properties were characterized in detail by X-ray diffraction, N₂ physisorption, H₂ temperature-programmed reduction, NH₃ temperature-programmed desorption, and Raman spectroscopy analyses. Results showed DCM combustion activity over V-Ni/TiO₂ catalyst was superior to that of V₂O₅/TiO₂ and NiO/TiO₂ catalysts. DCM could be completely converted into CO₂, HCl, and a little amount of CO over Ni-V/TiO₂ catalyst at 350 °C, the toxic by-products, such as CH₂Cl, aldehydes and phosgene could not be observed by online IR spectroscopy. The high catalytic activity, selectivity, and stability of V-Ni/TiO₂ catalyst could be due to the good oxidative dehydrogenation ability (ODH), the good reducibility of active oxygen species, and suitable strength of Lewis acidic sites upon introduction of nickel oxide.

1. Introduction
Chlorinated volatile organic compounds (CVOCs) such as dichloromethane (DCM) and trichloroethylene (TCE) are commercially produced and used for many purposes in different industries. Almost all CVOCs emitted are hazardous to the environment and public health; thus, stricter emission ceilings for each country are set. Catalytic abatement of CVOCs is an efficient, cost-effective, and environmentally sound way to abate these harmful emissions because of low energy consumption, high efficiency, and selectivity.¹,² Catalyst is undoubtedly the key factor to implement this technique. Generally, most reported catalysts for CVOC combustion are supported noble metals,¹³ transition metal oxides,¹⁴ and zeolites.⁵⁻⁷,¹² The ultimate aim of CVOCs catalytic combustion is to completely transform these hazardous materials into environmentally harmless compounds, such as H₂O, CO₂, and HCl. However, almost all catalysts are influenced by chlorine species produced by CVOCs decomposition. The interaction of catalysts with chlorine species usually leads to the catalyst’s partial or complete deactivation, which further results in crystallite growth (sintering and agglomeration), carbon deposition, change in physical properties, poisoning by chlorine species, and leaching out of active phase.⁶,⁷,¹³ The catalyst applied in CVOCs destruction should be not only highly active and selective at relatively low temperature, but also maintain high resistance to chlorine and its derivatives.¹⁴,¹⁵

Vanadium-containing catalysts are always shown to have good stability in Cl₂-HCl atmosphere. Especially, vanadia supported on TiO₂ are reportedly superior to the other conventional carriers such as Al₂O₃ and SiO₂ in several redox reactions because of the strong metal-support interactions (SMSI), which could improve the activity of surface oxygen on the catalyst. Even more interesting is the performance of V₂O₅/TiO₂ catalyst, which can be significantly changed by doping some other metal oxides as impurities or promoters.¹⁷,¹⁸

Monochloromethane (MCM) is usually a main by-product derived from the interaction of methoxy species and HCl in DCM combustion.⁷,¹⁰ MCM is more recalcitrant than DCM because of its low electrophilicity in central carbon atom. Thus, the transformation of MCM is more difficult than that of DCM.²⁰ Nickel-supported catalyst usually shows good oxidative dehydrogenation and hydrodehalogenation ability in many redox reactions.²¹,²² In the present work, a catalyst with vanadium–nickel mixed oxides supported on TiO₂ was prepared and used for DCM combustion; our aim is to investigate the selectivity, activity and stability of the catalyst in DCM combustion at relatively low temperature range. To the best of our knowledge, this catalyst has not yet been reported for use in DCM combustion.

2. Experimental
2.1 Catalyst preparation
The catalyst with vanadium–nickel mixed oxides supported on TiO₂ was prepared by conventional impregnation method. In a typical procedure, a certain amount of the precursors NH₄VO₃ (Shanghai SSS Reagent Co., Ltd), Ni(NO₃)₂·6H₂O (Shanghai Qingong Inorganic Co., Ltd), and oxalic acid were dissolved in deionized water under magnetic stirring at 60 °C.

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Then, 2.0 g of TiO2 support (Nanjing Haitai Nano materials Co., Ltd) was added to the solution under vigorous stirring for 20 min. After dehydrating the slurry in a rotary evaporator at a 70 °C water bath, the residues were dried at 110 °C for 12 h, and finally calcined in air at 500 °C for 5 h in a muffle furnace. The nominal loaded active phase of the as-prepared catalyst was 3% weight of vanadium atoms and 7% weight of nickel atoms, respectively, corresponding to the monolayer/submonolayer of mixed oxides on TiO2 support16, 23, and the as-prepared catalyst was denoted as V-Ni/TiO2 hereafter. For comparison, NiO/TiO2 and V2O5/TiO2 catalysts loaded with 10% nickel and vanadium, respectively, were prepared in the same way as aforementioned.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on an X’Pert Pro powder diffractometer using Cu Ka (λ = 0.154056 nm) radiation (40 kV and 30 mA). The diffractograms were recorded within 2θ = 10°–80° with a step size of 0.02° and a step time of 10 s. Crystal sizes were calculated using the Scherrer equation: 

\[ d = \frac{0.92 \lambda}{B \cos \theta} \]

where d is the crystal particle diameter (Å), λ is the wavelength (Å), B is the broadening of diffraction line measured at half its maximum intensity (radians), and θ is the reflection angle (radians). The nitrogen adsorption and desorption isotherms were recorded on an X'Pert Pro powder diffractometer using Cu Ka radiation (40 kV and 30 mA). The maximum intensity (radians), and θ is the reflection angle (radians). The nitrogen adsorption and desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2010 in a static mode. All samples were outgassed at 250 °C for 3 h before measurement. The specific surface area was calculated using the BET model. H2 temperature-programmed reduction (H2-TPR) was investigated on FINE SORB-3010 instrument by heating 200 mg of samples in H2 (10 vol. %)/Ar flow (30 mL min-1) at a heating rate of 10 °C/min from 50 to 900 °C. All samples were heated in highly pure Ar flow at 200 °C for 1 h and then cooled to 50 °C before measurement. NH3 temperature-programmed desorption (NH3-TPD) was performed on FINE SORB-3010 instrument equipped with a TCD. Prior to ammonia adsorption, the samples (100 mg) were pretreated in highly pure He stream (35 mL min-1) at 500 °C for 1 h. After cooling down to 50 °C, the samples were exposed to a flow of 20 vol. % NH3/He mixture (30 mL min-1) for 1 h and subjected to He flow for 1 h to remove physically bound ammonia. Finally, desorption performance was examined in He flow (30 mL min-1) from 50 °C to 500 °C at a heating rate of 10 °C/min-1. Raman spectra were obtained on a Raman spectrometer (HR 800 Lab Ram, Horiba Jobin Yvon, Villeneuve d’Ascq, France) equipped with a 531.95 nm Ar+ ion laser (frequency-doubled Nd: YAG, 20 mW) and CCD detector (multichannel, air cooled). The sample cell was purged with He stream for 30 min before pyridine adsorption, and then 100 µL pyridine was injected. The sample was exposed to the pyridine vapor for at ambient temperature for 30 min, and then purged with He for another 30 min to remove the physisorbed pyridine before measurement. The carbon deposition of the aged V-Ni/TiO2 after the stability test was investigated in TEM (Philips-FeI, Tecnai G2 F30 S-Twin). The sample was dispersed in absolute alcohol, and then supported on copper grid before observation.

2.3 Catalytic activity test

Catalytic experiments were performed in a fixed bed tubular reactor (quartz glass; 10 mm i.d.) at atmospheric pressure. 0.2 g of catalyst was placed in the middle of the reactor and diluted with 0.8 g of quartz sand. Both ends of catalyst bed were packed with quartz wool to prevent the catalyst from draining off. DCM feed gas was generated by bubbling the air (20.8% O2 and 79.2% N2) at a suitable flow rate through a saturator in ice bath, and a bypass flow of air was used to balance the total flow rate that gave the desired gas hourly space velocity (GHSV) in the catalyst bed. The feed DCM concentration was kept constant at 1000 ppm with a corresponding GHSV of 15000 mL g-1 h-1 in all experiments. All gas flow was controlled with mass flow controllers (Beijing Seven-star Electronics Co., Ltd). The effluent gases were analyzed online with an FT-IR spectrometer (Vertex 70; scan rate = 32 scans s-1; resolution = 2.5 cm-1) and a GC-9790 gas chromatograph equipped with FID and TCD. A Propak Q column was used to separate CO2 and organic compounds, whereas CO separation was achieved using a 5 Å molecular sieve column. The concentration of CH4 and CO2 and organic compounds, whereas 

3. Results and discussions

3.1 Catalytic activity results

![](image)

Fig. 1. Light-off curves of DCM over as-prepared catalysts. Gas composition: 1000 ppm DCM in air, GHSV=15000 mL g h-1. Fig. 1 shows that complete DCM conversion was achieved between 350 and 450 °C for all investigated samples. The V-Ni/TiO2 bi-component sample showed better performance than the mono-component ones and completely converted DCM at a lower temperature. The T50 value (temperatures with 90% DCM conversion achieved) of V-Ni/TiO2 was only 290 °C, about 140 °C lower than that of NiO/TiO2 and V2O5/TiO2 samples (T50 were about 433 °C), which was superior to that of some noble metal catalysts in the same conditions1, 2.

High conversion at low temperature is not the only criterion in identifying a good DCM combustion catalyst; product selectivity is also very important because poor selectivity may result in more toxic and recalcitrant by-products than the original reactant. Thus, the product selectivity of V-Ni/TiO2 catalyst for DCM combustion was investigated through online IR spectroscopy analysis at different temperatures.

Fig. 2 shows an absorption band at 2360 cm-1 with a shoulder at 2343 cm-1 is attributed to the asymmetric stretching vibration of CO2; meanwhile, the band at 680 cm-1 is ascribed to the deformation vibration of CO2. Doublet at 2173 and 2116 cm-1 are usually attributed to the stretching vibration CO. The weak thin bands at 3100–2700 cm-1 indicate the presence of HCl in gas phase1. Moreover, the bands located at
763 cm\(^{-1}\) are the stretching vibration of C–Cl bond, also the bands at 1276 and 1260 cm\(^{-1}\) are attributed to the twisting vibration and wagging vibration of methylene group in DCM molecule, respectively. Indeed, as informed from Fig. 2, the intensity of absorption bands of CO\(_2\) and HCl significantly increased as compared with that of CO with the reaction temperature increased, while the intensity of absorption bands corresponding to DCM gradually decreased and completely disappeared at 350 °C. It should be mentioned that the bands located at 1750–1700 cm\(^{-1}\) are the stretching vibration of C=O bond, also the bands at 1276 and 1260 cm\(^{-1}\) are attributed to the twisting vibration and wagging vibration of methylene group in DCM molecule, respectively. Indeed, as informed from Fig. 2, the intensity of absorption bands of CO\(_2\) increased reaction temperature further increased, which is much different from the quasi-steady conversion of DCM over NiO/TiO\(_2\) catalyst. The main products of all investigated samples were CO, CO\(_2\), HCl, and CH\(_2\)Cl. However, their distributions were far from identical, depending on the used catalysts. Using V\(_2\)O\(_5\)/TiO\(_2\), DCM conversion yielded a larger amount of CH\(_2\)Cl compared with Ni contained catalysts at low temperatures (below 300 °C). However, the yield of CH\(_2\)Cl obviously decreased and the selectivity of CO and HCl significantly increased with DCM conversion using NiO/TiO\(_2\) catalyst. Using V-Ni/TiO\(_2\), the main products of DCM conversion were CO\(_2\) and HCl, and the selectivity exceeded 95% and 90%, respectively, at 350 °C. A little amount of CO was also detected when DCM conversion was performed on V-Ni/TiO\(_2\) catalyst, and the yield of CO increased from 20 ppm to 51 ppm with increased temperature from 200 °C to 350 °C, and the results are consistent with that of IR spectra.

3.2 characterization results of catalysts
3.2.1 XRD results
The XRD patterns of as-prepared samples are shown in Fig. 4; corresponding crystallite sizes are listed in Table 1. It is informed from Fig. 4 that the characteristic diffraction peaks of tetragonal anatase TiO\(_2\) (PDF 65-5714) appeared on all investigated samples, also the feature diffractions of NiO (PDF 65-2901) appeared on NiO/TiO\(_2\) and V-Ni/TiO\(_2\) samples with different intensity. For V\(_2\)O\(_5\)/TiO\(_2\) sample, the characteristic peaks of V\(_2\)O\(_5\) (PDF 41-1426) can be observed, suggesting the formation of bulk V\(_2\)O\(_5\) on the surface of TiO\(_2\). However, there are no reflections of crystalline V\(_2\)O\(_5\) presented on V-Ni/TiO\(_2\) sample, indicating a relatively homogeneous dispersion of V\(_2\)O\(_5\) on the catalysts, or the particles are too small to be identified by the conventional X-ray diffraction method. As shown in Table 1, the crystalline sizes of V-Ni/TiO\(_2\) sample is much smaller than that of V\(_2\)O\(_5\)/TiO\(_2\), suggesting the introduction of nickel decrease the average crystalline sizes of TiO\(_2\) NPs, by providing dissimilar boundaries and suppressing the mass transportation, similar results are also reported by Li et al. The result is consistent with that of N\(_2\) physisorption, as the specific surface area of V-Ni/TiO\(_2\) was also increased with nickel oxide introduced.
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NiO/TiO₂ reducibility of as-prepared catalysts. As presented in Fig. 5, TPR of bulk NiO and surface free NiO species different nickel species. The peak located in about 344 °C with vanadia on TiO₂ ascribed to the reduction of bulk vanadia and highly dispersion participated along with V\(^{5+}\) partially overlapped reduction peaks located at 295 °C and 356 °C, respectively. The low temperature peak could be related to the reduction of different nickel species. The peak located in about 344 °C with a weak shoulder in 284 °C could be attributed to the reduction of bulk NiO and surface free NiO species \(^{22,27}\). It is reported that the reduction of NiO and inter-diffusion of NiO and TiO₂ are competitive processes, thus, the peak in about 398 °C could be assigned to the reduction nickel titanate phase \(^{22}\). The broad feature between 500 °C and 800 °C could be attributed to titanium ions transported to the surface of nickel crystallites by a bulk diffusion mechanism \(^{22}\). V₂O₅/TiO₂ showed a strong reduction peak at 515 °C with a shoulder around 447 °C, TiO₂ support is known to be reduced at the temperature higher than 540 °C \(^{3}\), thus, the peaks at 447 °C and 515 °C could be ascribed to the reduction of bulk vanadia and highly dispersion vanadia on TiO₂ support \(^{4,28}\). The V-Ni/TiO₂ mainly showed two partially overlapped reduction peaks located at 295 °C and 356 °C, respectively. The low temperature peak could be related to the reduction of highly dispersed NiO-like surface species participate along with V\(^{5+}\) \(^{29}\). For the inter-diffusion of NiO and TiO₂ occurs during reduction, the presence of sub-surface nickel species formed by the diffusion of nickel ions into TiO₂ support is very probable \(^{22}\). The high temperature reduction peak could be assigned to the reduction nickel titanate phase as discussed above. As informed from Fig. 5, all reduction peaks corresponding to vanadia and nickel oxide on V-Ni/TiO₂ sample shifted to lower temperature range as nickel oxide introduced, indicating that the interaction between nickel species and vanadium species can improve the reducibility of oxygen species on the surface of this catalyst, which would be beneficial for the destruction of DCM and its intermediates, since the catalytic activities of all investigated samples are basically in line with their redox properties (shown in Fig. 1).

3.2.2 H\(_₂\)-TPR results

H\(_₂\)-TPR experiments were performed to investigate the reducibility of as-prepared catalysts, as presented in Fig. 5, TPR of NiO/TiO₂ mainly exhibits two partially overlapped reduction peaks below 400 °C and a broad feature between 500 °C and 800 °C or higher. Since Ni\(^{5+}\) species are usually reduced to NiO without formation of intermediates, thus, the reduction peaks in NiO/TiO₂ sample could be assigned to the reduction of different nickel species. The peak located in about 344 °C with a weak shoulder in 284 °C could be attributed to the reduction of bulk NiO and surface free NiO species \(^{22,27}\). It is reported that the reduction of NiO and inter-diffusion of NiO and TiO₂ are competitive processes, thus, the peak in about 398 °C could be assigned to the reduction nickel titanate phase \(^{22}\). The broad feature between 500 °C and 800 °C could be attributed to titanium ions transported to the surface of nickel crystallites by a bulk diffusion mechanism \(^{22}\). V₂O₅/TiO₂ showed a strong reduction peak at 515 °C with a shoulder around 447 °C, TiO₂ support is known to be reduced at the temperature higher than 540 °C \(^{3}\), thus, the peaks at 447 °C and 515 °C could be ascribed to the reduction of bulk vanadia and highly dispersion vanadia on TiO₂ support \(^{4,28}\). The V-Ni/TiO₂ mainly showed two partially overlapped reduction peaks located at 295 °C and 356 °C, respectively. The low temperature peak could be related to the reduction of highly dispersed NiO-like surface species participate along with V\(^{5+}\) \(^{29}\). For the inter-diffusion of NiO and TiO₂ occurs during reduction, the presence of sub-surface nickel species formed by the diffusion of nickel ions into TiO₂ support is very probable \(^{22}\). The high temperature reduction peak could be assigned to the reduction nickel titanate phase as discussed above. As informed from Fig. 5, all reduction peaks corresponding to vanadia and nickel oxide on V-Ni/TiO₂ sample shifted to lower temperature range as nickel oxide introduced, indicating that the interaction between nickel species and vanadium species can improve the reducibility of oxygen species on the surface of this catalyst, which would be beneficial for the destruction of DCM and its intermediates, since the catalytic activities of all investigated samples are basically in line with their redox properties (shown in Fig. 1).

3.2.3 NH\(_₃\)-TPD results

The acidic properties of Catalyst were found to have significantly influence on the activity in CVOCs oxidation. The strength and amount of acidic sites were reflected in the desorption temperature and in the peak area of a plot of temperature-programmed desorption of NH₃ (NH₃-TPD). The surface acidic natures of all investigated samples are shown in Fig. 6. In all cases, a wide desorption peak could be seen in the temperature range of 100–500 °C, which could be fitted into three peaks through deconvolution. The sites retaining NH₃ at higher temperature than 275 °C could be assigned to strong acidic sites \(^{30}\), also the desorption peaks located at ~250 °C and ~150 °C indicate that the samples possess medium acidic sites and weak acidic sites \(^{31}\), respectively. As informed from Fig. 6, only weak and medium acidic sites presented on V₂O₅/TiO₂, however, both of weak, medium and strong acidic sites could be observed on NiO/TiO₂ and V-Ni/TiO₂ with different intensity. It is generally accepted that the medium and strong acidic sites are active sites in CVOCs oxidation. Compared with V₂O₅/TiO₂ and NiO/TiO₂, the medium and strong acidic sites over V-Ni/TiO₂ were much stronger, which would be beneficial for the destruction of DCM \(^{32}\).
strong Raman absorption bands at 636, 514, and 394 cm\(^{-1}\) could be ascribed to \(E_g\), \(A_{1g}+B_{1g}\), and \(B_{1g}\) vibration modes in TiO\(_2\) (anatase) \(^{33, 34}\). Generally, the bulk vanadium at low concentration resulting from V=O bond was prevalently located at around 1030 cm\(^{-1}\) in Raman spectra \(^{35}\). The V\(_2\)O\(_5\)/TiO\(_2\) catalyst exhibited two weak absorption bands at 1030 and 993 cm\(^{-1}\), which could be attributed to the vibration of terminal V=O bond stretch and V=O\(_5\) microcrystalline \(^{36}\), respectively, the result is consistent with that of XRD pattern. For V-Ni/TiO\(_2\) sample, the characteristic bands of V=O bond could not be observed, however, a band located at about 822 cm\(^{-1}\) could be attributed to the V-O stretching modes in Ni\(_2\)V\(_4\)O\(_8\) \(^{37, 38}\). The formation of Ni\(_2\)V\(_4\)O\(_8\) on V-Ni/TiO\(_2\) is consistent with the phase diagrams of NiO-V\(_2\)O\(_5\) system \(^{39}\). Since this compound cannot be observed in XRD pattern, probably it is presented in an amorphous form on the surface of V-Ni/TiO\(_2\), or the particle sizes are too small to be identified by the conventional X-ray diffraction method. The coexistence of Ni\(_2\)V\(_4\)O\(_8\) and NiO can also favor the specific surface area of V-Ni/TiO\(_2\) \(^{40}\), as shown in Table 1. Raman peaks located at about 473 cm\(^{-1}\) and 550 cm\(^{-1}\) are usually attributed to the Ni–O bond bending vibrations and stretching vibrations \(^{41, 42}\), respectively; these peaks could not be clearly observed since they are overlapped with the strong vibration modes of TiO\(_2\) (anatase).

The acidic natures of as-prepared samples are also investigated by Raman spectra after pyridine adsorption, and the results are shown in Fig. 8.

As can be seen, the V-Ni/TiO\(_2\) sample showed two absorption bands at 991 and 1030 cm\(^{-1}\), which could be attributed to the U\(_1\) and U\(_{12}\) modes of ring-breathing vibrations (UCCN) of liquid pyridine \(^{43, 44}\), corresponding to physically adsorbed pyridine. The strong absorption band at 1016 cm\(^{-1}\) in V-Ni/TiO\(_2\) and NiO/TiO\(_2\) samples, was due to the U\(_1\) mode of ring-breathing vibration (UCCN), resulting from pyridine coordination to Lewis acidic sites \(^{44, 45}\). The absorption band at 3077 cm\(^{-1}\) in V-Ni/TiO\(_2\) sample could be ascribed to pyridine adsorbed on Lewis acidic sites overlapping with hydrogen bonded pyridine \(^{43}\).

4. Stability test of catalysts

The stability of catalysts in DCM combustion was investigated in a 100 h continuous test at 300 °C. As shown in Fig. 9, all samples showed good stability during long-term test. DCM conversion could be maintained above 99% over V-Ni/TiO\(_2\) catalyst, no deactivation phenomenon could be observed. It is generally accepted that both the reducibility and acidic properties are responsible for the performance of transition metal oxide catalysts in CVOCs oxidation \(^{46}\). As informed from Fig. 6, the strength and the amount of medium and strong acidic sites on V-Ni/TiO\(_2\) were more than those on V\(_2\)O\(_5\)/TiO\(_2\), which would be beneficial for the destruction of DCM and the intermediates. However, the NiO/TiO\(_2\) sample with the comparative medium and strong acidic sites didn’t show corresponding activity as V-Ni/TiO\(_2\), this means the reducibility of catalyst may also play an important role in DCM oxidation. As shown in Fig. 5, the V-Ni/TiO\(_2\) sample showed better reducibility than the NiO/TiO\(_2\) and V\(_2\)O\(_5\)/TiO\(_2\) samples, also the co-existence of Ni\(_2\)V\(_4\)O\(_8\) and NiO (shown in Fig. 7 and Fig. 4, respectively) on the surface of V-Ni/TiO\(_2\) also favoured the oxidative dehydrogenation ability of V-Ni/TiO\(_2\) \(^{40}\), thus, the V-Ni/TiO\(_2\) showed good activity during long term exposure to the DCM.

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5. TEM of V-Ni/TiO$_2$ catalyst

For nickel-rich catalyst, the carbon deposit is very probable during the long-term running in DCM oxidation, thus, the morphology of fresh and used V-Ni/TiO$_2$ (after 100 h continuous test) were observed in TEM, as shown in Fig. 10. No significant differences could be observed between the fresh and aged samples, also no filamentous carbon could be observed on the surface of aged sample $^{47}$, suggesting a high coke resistance ability of V-Ni/TiO$_2$ catalyst.

Table 2. Some work made on total oxidation of DCM with transition metal oxide catalysts

<table>
<thead>
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<th>Ref.</th>
<th>Catalyst(s) used</th>
<th>DCM content /ppm</th>
<th>GHSV /h$^{-1}$</th>
<th>$T_{\text{ox}}$/°C</th>
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<tbody>
<tr>
<td>35</td>
<td>4Ce1Cr</td>
<td>1000</td>
<td>15000</td>
<td>335</td>
</tr>
<tr>
<td>4</td>
<td>V$_2$O$_5$/Al$_2$O$_3$-TiO$_2$</td>
<td>500</td>
<td>32000</td>
<td>420</td>
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<tr>
<td>9</td>
<td>Ru7%Ce-Al$_2$O$_3$</td>
<td>700</td>
<td>10000</td>
<td>260</td>
</tr>
<tr>
<td>48</td>
<td>CoCr$_2$O$_4$-4</td>
<td>300</td>
<td>15000</td>
<td>257</td>
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<tr>
<td>49</td>
<td>CeZr</td>
<td>1000</td>
<td>71 m$^3$ kg$^{-1}$ h$^{-1}$</td>
<td>467</td>
</tr>
<tr>
<td>46</td>
<td>VO$_x$/TiO$_2$-SG</td>
<td>1000</td>
<td>15000</td>
<td>313</td>
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<tr>
<td>This work</td>
<td>V-Ni/TiO$_2$</td>
<td>1000</td>
<td>15000 mJ g$^{-1}$ h$^{-1}$</td>
<td>290</td>
</tr>
</tbody>
</table>

It should be mentioned that it is very difficult to compare the results of our work with those reported in the literatures, since the activity of the tested catalysts significantly related to the operation conditions used. As listed in Table 2, the activity of V-Ni/TiO$_2$ sample is superior to most of catalysts listed, such as 4Ce1Cr, V$_2$O$_5$/Al$_2$O$_3$-TiO$_2$, CeZr mixed oxide and VO$_x$/TiO$_2$-SG, only inferior to that of Ru7%Ce-Al$_2$O$_3$ and CoCr$_2$O$_4$-4.

6. Plausible mechanism for DCM decomposition over V-Ni/TiO$_2$ catalyst

It is reported by Gai et al.$^{50}$ that the presence of oxygen vacancies associated with the Lewis acidic centers of catalyst, DCM could be adsorbed on these oxygen vacancies in two ways through the relatively negative chlorine at low temperature.$^{51}$ One is bridge–bounded DCM, in which DCM is adsorbed through the two chlorine atoms (1). The other is line–bounded DCM; in this case, DCM is adsorbed through a chlorine apex (2). The adsorbed DCM could be attacked by the adjacent nucleophilic [O] (O$^-$ and/or O$^{2-}$) species, the two chlorine atoms are substituted by oxygen atoms analogous to S$_2$O$_2$ reaction, leading to the surface absorbed species (3) and formaldehyde species (4). The Cannizzaro reaction between (3) and (4) give the adsorbed formate species (5) and methoxy species (6)$^{51}$. The mixture of vanadia and nickel oxide modified not only the redox properties of the system but also the acid–base characters of the oxygen species on V-Ni/TiO$_2$ catalyst$^{48}$, as shown in Fig. 6 and Fig. 8, respectively; as well as the coexistence of NiO and Ni$_2$V$_2$O$_7$ on V-Ni/TiO$_2$ catalyst with p-type semiconductor nature promotes its oxidative dehydrogenation ability$^{48}$, thus, the complete destruction of DCM and its intermediates could be attained at a lower temperature as compared with the other two mono-component catalysts. Based on the above discussions, a plausible reaction mechanism can be proposed for catalytic combustion of DCM over V-Ni/TiO$_2$ catalyst, as shown in Fig. 11.

7. Conclusions

V$_2$O$_5$ and/or NiO modified TiO$_2$ (anatase) catalysts were prepared by impregnation method and investigated in catalytic combustion of DCM. Both acidic and redox properties play important roles in deep oxidation of DCM. V-Ni/TiO$_2$ exhibits the best activity and stability for the model compound selected. The coexistence of NiO and Ni$_2$V$_2$O$_7$ good reducibility and oxidative dehydrogenation ability, as well as high intensity of medium and strong Lewis acidic sites and high coke resistance ability of the catalyst, are responsible for the destruction of DCM and its intermediates at low-temperature range; therefore, the V-Ni/TiO$_2$ catalyst shows good stability during long term exposure to DCM.

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Notes and references
